Physico-Chemical Studies on Molecular Compounds. III. Vapor Pressures of Diphenyl, 4, 4'-Dinitrodiphenyl, and Molecular Compound between Them

By Syûzô SEKI and Keisuke SUZUKI

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Introduction

In a previous paper,[1] we have reported the vapor pressures of quinhydrone and of the molecular compound between hexamethylbenzene and picryl chloride. These molecular compounds (M. C.'s for brevity) are constructed with (1:1) molar ratio of the component molecules, and the benzene nuclei of them are arranged in nearly parallel positions alternately. Now, there are recently known some M. C.'s which are considerably different from those in the molecular arrangement as well as in their composition. According to James, Saunder, and others,[2] 4,4'-dinitrodiphenyl (D. N. D. for brevity) forms a number of M. C.'s with diphenyl and its derivatives. Their general type of crystal structure stands in contrast in such points as that the component molecules are packed in nearly perpendicular positions to each other and that the molar ratios differ from M. C. to M. C., giving no (1:1) molar ratios. In these respects, it will be of some interest to study the present materials in comparison with the substances already reported and also in relation to the urea-adducts[3] having some resemblance in their molecular arrangements, as well as to the molecular sieve actions of some zeolite crystals.[4]

Experimental

Apparatus.—The vapor pressures as well as the variations of composition of the solid phase as the evaporation proceeds were measured by the effusion method. The details of the apparatus were already reported in a previous paper,[5] so that its description may be omitted here.

Samples.—*Diphenyl*: The product "Zur Analyse" of Dr. Theodor Schuchart was recrystallized from glacial acetic acid solution. m. p. 69.5°~69.8°C.

D. N. D.: The material was prepared through nitration of diphenyl with fuming nitric acid, and then the product was recrystallized once from ethyl alcohol and further twice from acetone, finally being subjected to fractional sublimation under high vacuum (10^{-5} mm. Hg.) at about 120°C. m. p. 237.0°~237.5°C.

M. C. (1:3): Two acetone solutions containing diphenyl (somewhat in excess of the calculated 1:3 ratio) and D. N. D. were mixed at a little below the boiling point and then M. C. was precipitated by slow cooling of the mixture at a rate of about 10°C./hour. m. p. 194°~225°C.* The reason for such a wide range of melting process will be explained in a later section.

Results

The vapor pressures of diphenyl and D. N. D. are given in Tables 1 and 2 and illustrated in Fig. 1. The vapor pressure equations derived from them are also given in the bottoms of each table. The relation of the vapor pressures of (1:3) M. C. (vapor pressures

Table 1
Vapor Pressure Values of Diphenyl

t°C.	$P_{mm.Hg.} \times 10^3$
14.3	2.33
14.8	2.38
16.8	3.16
19.7	4.19
22.0	5.44
23.8	6.44
25.6	7.78
27.6	9.23
28.0	9.44
29.9	11.9
31.3	13.8
34.1	17.4

$$\log P = 11.003 - 3918.2/T$$
$$T = 273.14 + t$$

(1) I. Nitta, S. Seki, H. Chihara and K. Suzuki, *Sci. Papers Osaka Univ.*, No. 29 (1951).
(2) (a) W. S. Rapson, D. H. Saunder and E. T. Stewart, *J. Chem. Soc.*, **1946**, 1110; (b) D. H. Saunder, *Proc. Roy. Soc.*, **A190**, 508 (1947); (c) J. M. van Niekerk and D. H. Saunder *Acta Cryst.*, **1**, 44 (1948); (d) R. W. James and D. H. Saunder, *Proc. Roy. Soc.*, **A190**, 518 (1947).
(3) A. E. Smith, *Acta Cryst.*, **5**, 224 (1952).
(4) R. M. Barrer, *Quart. Rev.*, **3** 293 (1949).
(5) I. Nitta, S. Seki, M. Momotani and K. Sato, *J. Chem. Soc. Japan*, **71**, 278 (1950).

* Rapson et. al. 191°~221°C. see ref. (2a).

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Table 2
Vapor Pressure Values of D. N. D.

t°C.	Pmm.Hg.$\times 10^3$
138.1	2.92
139.7	3.85
140.5	3.49
143.2	4.38
146.0	5.04
148.1	6.15
150.3	7.10
152.3	8.60
155.3	9.72

$\log P = 10.744 - 5458.2/T$

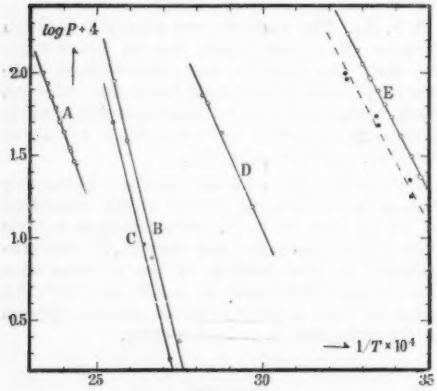

Fig. 1.—Vapor pressures of D. N. D. (A), (1:6) M. C. (B and C), (1:3) M. C. (D), and Diphenyl (E)
dotted line: Bright's values

calculated from the effusion velocity through an orifice of unit area) with the variation of effused amount are shown in Fig. 2. At relatively lower temperatures (e. g. curve (a) at 63.7°C. in the figure), the curves are composed of two regions: In the initial part, the vapor pressures are almost constant up to about 4.5% of the effused amounts, and then decrease remarkably. The position of the point B, at which the velocity begins to slow down, is more distinct at lower temperatures. But, as the temperature rises, the horizontal part (A-B) begins to incline downwards and the position of B becomes less distinct, moving to a region of somewhat smaller amounts of effusion. It is confirmed by the experiments that the material evaporated in the region (A-C) consists entirely of diphenyl. It is by the introduction of its molecular weight into the effusion equation that the vapor pressures at various stages of effusion as shown in the Fig. 2 are obtained. Extrapolating the curve to the zero point of effusion, we obtained the

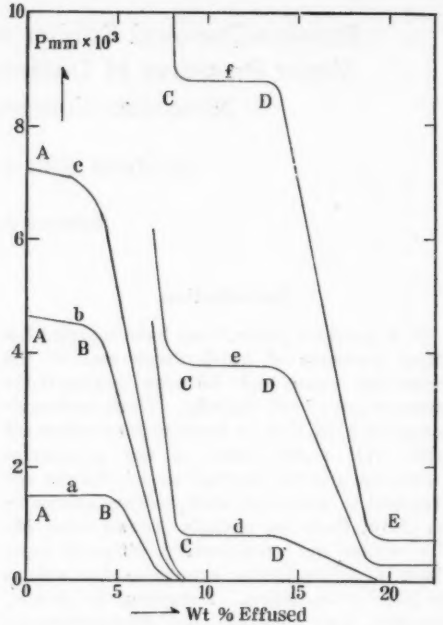

Fig. 2.—Vapor pressure change of M. C. with variation of effused amount
Experimental temperatures are as follows:
a: 63.7°C.; b: 74.5°C.; c: 79.9°C.;
d: 105.5°C.; e: 112.8°C.; f: 118.7°C.

Table 3
Vapor Pressure Values of (1:3) M. C.

t°C.	Pmm Hg.$\times 10^3$
63.7	1.54
74.5	4.33
79.9	7.14
81.6	7.36

$\log P = 10.722 - 4555.9/T$

vapor pressure data of (1:3) M. C. at the initial stage of sublimation as given in Table 3 and Fig. 1. As the vapor pressure is increased by raising the temperature of the experiment, there appears another horizontal portion in the region exceeding about 8% of the effused amount. This composition is corresponding to nearly (1:6) molar ratio and the constancy of vapor pressure implies the occurence of another new sort of M. C. By the microscopic observation of the sample at this stage of effusion (8%), it is found that the original (1:3) M. C. is completely converted into another sort of woolly small crystalline aggregate, which shows a distinct melting point (m. p. 210°C.).

As is evident from Fig. 2, this horizontal

portion (C-D) is not inclined as the temperature rises and the position of point D remains always at the constant value of abscissa (13±0.5%) within the experimental error. The large portion of the material effused in the region of (C∼D) is found to be diphenyl. Since the determinations of the composition of effused substances by chemical analysis is difficult on account of their small amount, we have estimated the composition of the solid phase and molecular weight of effused substances approximately in the following manner. Assuming that the partial vapor pressures of D. N. D. are equal to those of pure D. N. D. at the same temperatures, then the value of abscissa at which the diphenyl molecules contained in the solid phase is exhausted may be calculated to be 18.6% from the observed rate of effusion and original composition of (1:3) M. C, In fact, the point where the vapor pressures reach those of pure D. N. D. is found to be 18.7±0.3%, proving the adequacy of the above assumption.

On this basis, the vapor pressures of (1:6) M. C. are calculated as given in Table 4 and Figs. 1 and 2. It was found also that the vapor pressures of this M. C. are influenced by the history of their preparation. That is, the product prepared from the decomposition of fresh (1:3) M. C. shows higher vapor pressures (line B in Fig. 1 and (a) in Table 4) than those from the (1:3) M. C. stored for about a month in a desiccator (line C in Fig. 1 and (b) in Table 4). The values of thermodynamic functions derived from the vapor pressure data of all the specimens are given in Table 5.

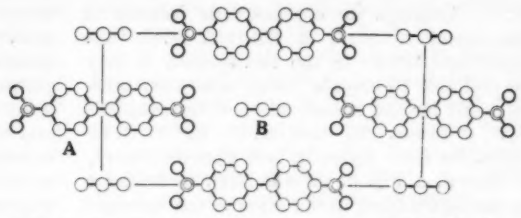

Fig. 3.—Idealized structure of a series of (1:3) M. C.
A: D. N. D. Molecules.
B: Diphenyl molecules or its derivatives.

Table 4
Vapor Pressure Values of (1:6) M. C.

(a)		(b)	
t°C.	$P_{mm.Hg.} \times 10^3$	t°C.	$P_{mm.Hg.} \times 10^3$
90.5	0.238	94.5	0.184
101.8	0.760	105.5	0.910
112.8	3.89	119.5	1.84
118.7	8.90		
$\log P = 18.361 - 8016.2/T$		$\log P = 18.987 - 8349.6/T$	

Although the final product beyond the point D shows the same Debye photograph as well as the same melting point with those of pure D. N. D., the vapor pressures are of a little higher values (not more than 5%) than the D. N. D. prepared by the ordinary method.*

Discussion

The results of vapor pressures obtained in the present investigation may be discussed first in comparison with the data already reported by other investigators. Among the substances measured by us, only the vapor pressure of diphenyl was measured by Wolf[6] and Bright.[7] The former reported merely a value of the heat of sublimation (16.4±0.2 kcal./mol.), which is considerably smaller than ours (17.9±0.4 kcal./mol.), while the heat of sublimation obtained by Bright(17.4±0.7 kcal./mol.) is in good agreement with ours, their vapor pressure values being, however, somewhat lower than ours as shown in Fig. 1.

Table 5
Enthalpy, Entropy and Standard Free Energy Changes of Sublimations*

Substances	ΔH kcal./mole	ΔS e. u./mole	$\Delta F^{298.1}$ kcal./mole
Diphenyl	17.94±0.41	37.14±1.36	6.89±0.81
(1:6) M. C. (a)	36.70±1.79	70.88±4.79	15.58±3.32
(1:6) M. C. (b)	38.23±0.70	73.75±1.86	16.24±1.25
(1:3) M. C.	20.86±0.41	35.90±1.44	10.15±0.84
D. N. D.	24.99±0.44	36.01±0.80	14.25±0.68

† The thermodynamic fuctions of M. C's are corresponding to those of their decomposition processes, in exact sense (see in the text).

* Similar facts were also found in the cases of α-quinol and picryl chloride produced by decomposition of the M. C.

(6) K. L. Wolf and H. Weghofer, *Z. Physik. Chem.* **B39**, 194 (1938).
(7) N. F. H. Bright, *J. Chem. Soc.*, **1951**, 626.

Now, we may proceed to the problems of M. C. Although the characteristic features of the crystal structure of the (1:3) M. C. were mentioned briefly in the last section, it may be desirable to explain them somewhat more in detail for the consideration of the evaporation processes. In this M. C., the D. N. D. molecules form layers in face-centered array, as shown in Fig. 3. The D. N. D. molecules A in the figure lying in this layer are so arranged that a gap is left between the nitro groups of adjacent D. N. D. molecules. By superposing such layers with a spacing of 3.5 A., these gaps will produce a set of tubular cavities, also in face-centered array, running through the whole structure. The molecules of diphenyl or its derivatives (B in Fig. 3) occupy these tubular cavities, as shown end-on in the figure. Thus the directions of the long axes of B molecules is exactly or nearly perpendicular to the layers containing D. N. D. molecules. The ratio of the number of B molecules to that of D. N. D. molecules varies from compound to compound, and depends on the length of B molecules rather than on their chemical nature, and, indeed, it has been found possible to predict the molar ratio in M. C. from a knowledge of such molecular length, indicating no localized bonding between A and B molecules. The non-integral ratio (1:3.33) of the M. C. with 4-chlorodiphenyl is the most remarkable example.[2a][2d]

Turning to the evaporation process of (1:3) M. C., we can find a situation similar to that of the two M. C.'s reported in the previous paper,[1] i. e. the preferred evaporation of the more volatile component occurs, and the vapor pressures, the compositions of gaseous as well as of crystalline phase change with the progression of evaporation. When examined in more detail, however, the behavior of the M. C.'s of the present series is different in several points. As shown in Fig. 2 the vapor pressure-composition curve has, instead of one in the cases of previously reported substances, two horizontal regions followed by more gently sloped region than the M. C.'s previously reported.

From the standpoint of phase rule considerations, the horizontal parts, the constant pressure regions, which are independent on the compositions (A-B and C-D), mean the coexistence of one gas and two solid phases, whereas the other sloping regions (B-C and D. E) mean the presence of one gas and one solid phase.

In the cases of M. C.'s reported in a previous paper[1] the evaporation of the more volatile component necessitates the collapse of the original mother crystals on account of the features of the molecular arrangements in which each of the component molecules are piled up alternately. Accordingly, when the molecules of a more volatile component evaporate, the less volatile component molecules must be separated from the original crystals and recrystallized at a considerably rapid rate. Indeed, we obtained a wider range of horizontal parts of vapor pressures in these M. C.'s, implying that adequate conditions for the coexistence of the two solid phases are realized easily.

On the other hand, in the present M. C. the selective evaporation of the more volatile component would not necessitate the collapse of the mother crystals on account of the above mentioned structural characteristics. Indeed, the first horizontal parts (A-B) do not cover so wide a region as that of the M. C. previously reported and tend to slope at higher temperatures (e. g. the curve at 79.9°C.). This sloping tendency means the formation of a solid-solution-like structure resulting from the violent thermal motions of B component molecules along the tubular cavities.

Similar curves have been found recently in the hydrogen-titanium system by A. D. Mc. Quillan.[8] In this system, the lattice structure of titanium changes, appearing in the three types of interstitial compounds of α, β and γ, as the amount of hydrogen in the solid phase increases. In the midway regions between the definite composition of these interstitial compounds, they also show a solid-solution-like behavior. As is well known, such a phenomenon is frequently observed also in the hydration process of some sorts of gels and other hydrates[9] in which so-called "vagabond waters" are contained.

The wide range of melting phenomena observed in the present (1:3) M. C. described in the second section may be attributed to the formation of a solid solution owing to the partial evaporation of diphenyl. The comparison of the ΔH value of the (1:3) M. C. in Table 4 with that of the component crystals indicates also that the interaction of each component is not greatly strengthened by the formation of M. C.

When the amounts of effusion exceed about 8% of the original weight which corresponds to the molar ratio of about (1:6), the vapor pressure again retains a constant value, implying the coexistence of the two new solid phases. The existence of this (1:6) M. C. has

(8) A. D. Mc. Quillan, *Proc. Roy. Soc.*, **A204**, 309 (1951).
(9) W. Eitel, "Physikalische Chemie der Silikate", 1941, S. 517.

not been known yet for D. N. D.-diphenyl system. Such a large deviation of molar ratio from (1:1) may be very scarce for crystalline M. C. of aromatic nitrocompound-aromatic hydrocarbon (or aromatic amine, phenol) systems.* The distinct melting point (see section 2), the invariance of the flatness of vapor pressure in the region (C-D) as well as the constancy of the position of point D at various temperatures, and the values of thermodynamic functions given in Table 3 may be looked upon as the evidences of the considerably stable structure of this (1:6) M. C. Although its crystal structure is not yet known, the mobility of the diphenyl molecule in this (C-D) region may be supposed to be restrained more strongly than the (1:3) M. C.

It is worth while to note, however, that the free energy of (1:6) M. C. prepared from two samples of the (1:3) M. C.'s which had been preserved for different periods of time, differs somewhat in each case. For the elucidation of this ageing effect, however, a further detailed investigation will be necessary.

In conclusion the authors wish to express their sincere thanks to Professor Nitta for his gracious encouragement and suggestions during this work. The expense of this investigation was defrayed from the funds of Taniguchi Kôgyô Shôreikai as well as from the Scientific Research Expenditure Grant from the Ministry of Education to which the authors' thanks are due.

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* It is known that the urea-adducts (see ref (3)), M. C. between desoxycholic acid and aliphatic long chain compounds (Y. Go and O. Kratky, *Z. Physik. Chem.*, **B26**, 439 (1934)), gas hydrate (W. F. Claussen, *J. Chem. Phys.*, **19**, 259 (1951); H. V. Stackelberg and H. R. Muller, *Naturwiss.*, **38**, 456 (1951) **39**, 20 (1952); L. Pauling and R. E. Marsh, *Proc. Nat. Acad. Art and Sci.*, Feb (1952)) and other so-called "clathrate compounds" (D. E. Powell, H. M. Powell, *J. Chem. Soc.*, **1947**, 208; **1948** 571, 815) show such anomalous molar ratio.

On the Harkins—Jura's Adsorption Isotherm and Its Constants.

By Tomohiko SAKAKI

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I. Introduction

W. D. Harkins and G. Jura[1] obtained experimentally the following equation of state for the condensed films spread on the surface of liquid:

$$\pi = b - a\sigma \qquad (1)$$

where π is the surface pressure, σ is the area per molecule of the film, and b and a are constants. They also found that the above linear relationship is applicable to adsorbed films on solids.

Equation (1) can be transformed into an adsorption isotherm expressed in terms of equilibrium pressure p and adsorbed volume v_a,

$$\log_{10}\frac{p}{p_0} = B - \frac{A}{v_a^2} \qquad (2)$$

with

$$A = \sigma\Sigma^2 V^2/2\times 2.303 NRT \qquad (3)$$

and

$$B = A/v_s^2$$

where Σ is the surface area of adsorbent, V the volume of one mole of ideal gas at N. T. P., N Avogadro number, p_0 the saturation pressure, and v_s the adsorbed volume at p_0.

Eq. (2) gives Type II isotherms which are in good agreement with the experimental curves up to $p/p_0=1/3$ or higher. Moreover, the surface area Σ is proportional to the square root of A;

$$\Sigma = kA^{1/2} \qquad (4)$$

Harkins and Jura regarded k in (4) as being characteristic to each adsorbate and independent of the adsorbents. Thus they have given the values of k to the four kinds of vapors, calculating from their isotherms on the anatase powder the area of which had been determined

(1) W. D. Harkins and G. Jura, *J. Am. Chem. Soc.*, **66**, 1366 (1944); *J. Chem. Phys.*, **11**, 430 (1943); ibid, **11**, 431 (1943).

Table 1

The H. J. Constants

Adsorbate	Temp. (°K)	k (m.²/cc.)	A (cc./gr.)[2](a)	CAT (cal./mole·1/cm.⁴)(b)	σ_0 (Å.²)(c)	CAT σ_0^2 (cal./mole)
N_2	77.4	4.01	11.8	$159. \times 10^{-30}$	16.2	417
H_2O	298.	3.83	12.9	$668. \times$ 〃	10.5	734
n-C_4H_{10}	278.	13.6	1.02	$48.4 \times$ 〃	32.1	499
n-C_7H_{16}	273.	16.9	0.664	$31.5 \times$ 〃	45.	640

(a) The value of 13.8 m.²/gr. was used for Σ.

(b) $C = \dfrac{N^2 R \ln_{10}}{V^2 \Sigma^2}$

(c) The values of σ_0 for water and n-butane were calculated from the liquid densities according to B. E. T.. The value for n-heptane was determined from crystallographic data. (See Reference (1)).

by the "absolute method"[2] (Table 1). It is possible, therefore, to estimate the surface areas of solids using Eqs. (2) and (4) and Table 1 from the adsorption isotherms of these vapors on the solids, without the assumption of a molecular area of the adsorbate. This is called the "relative method" by the original authors.

There are, however, a few ambiguous points in the above-mentioned theory of adsorption. First, though Eq. (2) is considered to be applicable to multimolecular adsorption, the theoretical basis for this is not obvious. Secondly the assumption that the values of k are independent of adsorbents should be examined in more detail.

II. Thermodynamic Considerations

We shall begin by considering an adsorbed film composed of N_A molecules of the vapor adsorbed on a crystalline solid surface, having equilibrium pressure p at T°K below the critical temperature. If the same vapor has the saturation pressure p_0 in equilibrium with its liquid (or solid) at T°K, the difference in molar free energy between the film and the liquid, $\bar{F}$ is given by

$$\bar{F} = RT \ln \frac{p}{p_0} \tag{5}$$

On the other hand $\bar{F}$ is formally written as

$$\bar{F} = (H_A - E_L) - T\bar{S} \tag{6}$$

where H_A is the molar differential enthalpy of adsorption, E_L the enthalpy of condensation per mole, and S the difference in the molar entropy between the two states.

From (5) and (6) we get

$$\ln \frac{p}{p_0} = -\frac{\bar{S}}{R} + \frac{1}{RT}(H_A - E_L) \tag{7}$$

Now H_A is the function of the adsorbed amount N_A, the form of which is determined experimentally. When $p \to p_0$, $H_A \to E_L$; hence $\bar{S}$ is a function of N_A as well, and approaches zero as p tends to reach p_0. If H_A and $\bar{S}$ are expressed as functions of N_A, $H_A(N_A)$ and $\bar{S}(N_A)$, the observed isotherm is

$$\ln \frac{p}{p_0} = -\frac{\bar{S}(N_A)}{R} + \frac{1}{RT}\{H_A(N_A) - E_L\} \tag{8}$$

For convenience, introducing v_a in place of N_A,

$$v_a = V \cdot N_A / N.$$

Eq. (8) can be written as

$$\ln \frac{p}{p_0} = -\frac{\bar{S}(v_a)}{R} + \frac{1}{RT}\{H_A(v_a) - E_L\} \tag{9}$$

The dimensional consideration leads to the fact that H_A and $\bar{S}$ are the functions of degree of coverage, θ, given by

$$\theta = N_A / N_0$$

where N_0 is the number of molecules adsorbed on the surface when it is covered with a complete monomolecular layer. Thus Eq. (8) is rewritten as

$$\ln \frac{p}{p_0} = -\frac{\bar{S}(\theta)}{R} + \frac{1}{RT}\{H_A(\theta) - E_L\} \tag{10}$$

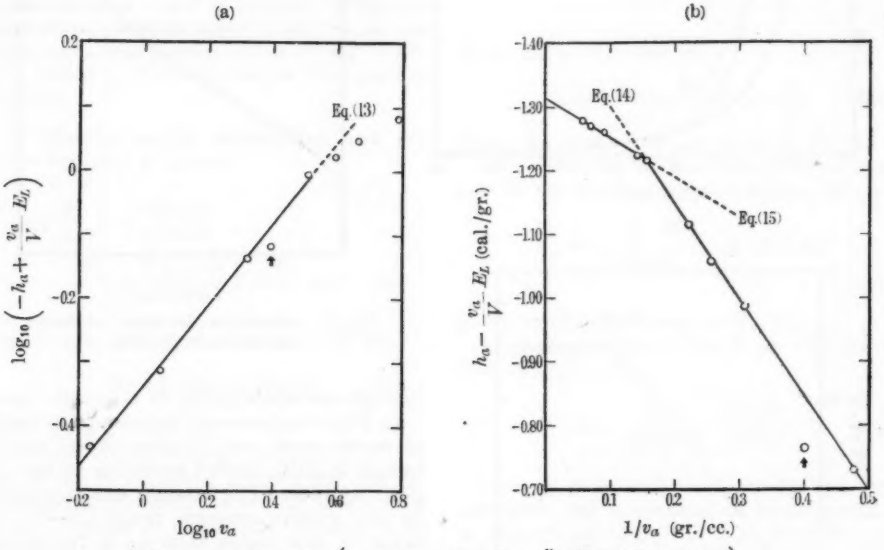
When the degree of coverage reaches θ, the work required to evaporate all the molecules of the film is

(2) W. D. Harkins and G. Jura, *J. Am. Chem. Soc.*, **66**, 1362 (1944).

Table 2

The Enthalpy Functions in the System of H_2O–Anatase

Range	Integral Enthalpy, h_a	Molar Differential Enthalpy, H_A
v_a, 0.68—3.25 cc./gr. p/p_0, 0 —0.10 〃	$h_{a1}=-0.461(v_a)^{5/6}+\frac{v_a}{V}E_L$ Eq. (13)	$H_{A1}=-6460(v_a)^{-3/6}+E_L$ Eq. (16)
v_a, 2.09—6.16 〃 p/p_0, 0.02—0.55 〃	$h_{a2}=-1.446+\frac{1.50}{v_a}+\frac{v_a}{V}E_L$ Eq. (14)	$H_{A2}=-\frac{33600}{v_a^2}+E_L$ Eq. (17)
v_a, 6.16—∞ 〃 p/p_0, 0.55—1.00 〃	$h_{a3}=-1.315+\frac{0.634}{v_a}+\frac{v_a}{V}E_L$ Eq. (15)	$H_{A3}=-\frac{14200}{v_a^3}+E_L$ Eq. (18)



The arrowed point $\left(v_a=2.49\text{ cc./gr.},\ h_a-\frac{v_a}{V}E_L=0.762\text{ cal./gr.}\right)$ lies neither on the line of (a) nor on that of (b).

Fig. 1.—The Variation of the Integral Enthalpy of Adsorption with v_a in the System of H_2O—Anatase

$$F_a=\frac{1}{N}\left\{-T\int_0^{N_A}\bar{S}(N_a/N_0)dN_A+\int_0^{N_A}H_A(N_A/N_0)dN_A+KN_A\right\} \quad (11)$$

where K is a constant.

By definition the surface pressure of the film is given by

$$\pi=-\left(\frac{\partial F_a}{\partial \Sigma}\right)_{T,\,N_A}=-\frac{1}{\sigma_0}\left(\frac{\partial F_a}{\partial N_0}\right)_{T,\,N_A} \quad (12)$$

π is calculated from the isotherm, using Eqs. (11) and (12).

III. The Isotherm and Heats of Adsorption in the System of H_2O—Anatase

Harkins and Jura[3] measured the heats of immersion into water of the anatase samples, on which various quantities of water vapor had been adsorbed. The integral enthalpies, h_a's, of this case are known from the results of this experiment.

The formulae listed in column 2 of Table 2 correctly represent the original data[4] written in terms of cals. per one gram of the adsorbent as illustrated in Fig. 1 (a) and (b). The variation of the molar differential enthalpy H_A with v_a, derived from these formulae, are

(3) W. D. Harkins and Jura, *J. Am. Chem. Soc.*, **66**, 919 (1944).

(4) Table I in the reference (3).

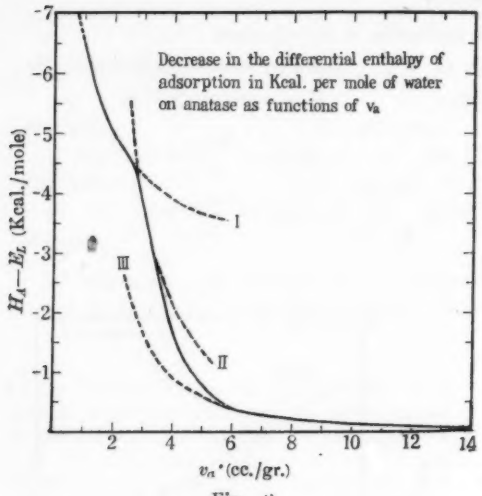

Decrease in the differential enthalpy of adsorption in Kcal. per mole of water on anatase as functions of v_a
$H_A - E_L$ (Kcal./mole)
v_a (cc./gr.)
I
II
III

Fig. 2.

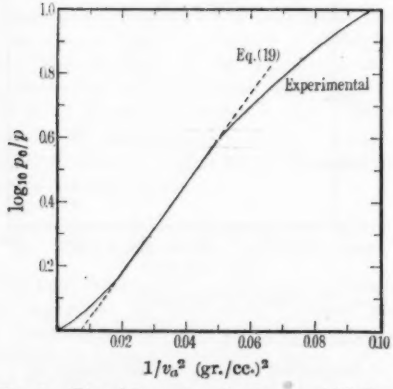


Fig. 3.—The Adsorption Isotherm of H_2O on Anatase Plotted According to H. J.

shown in Fig. 2 and column 3 of Table 2. In Fig. 2, curve I represents $H_{A1}(v_a)$, curve II $H_{A2}(v_a)$ and curve III $H_{A3}(v_a)$, respectively. It is to be noted that Eq. (13) is very similar to the empirical formula suggested by Lamb and Coolidge[5] on the integral heats of adsorption of various organic vapors on charcoal. As v_a is increased, $-H_{A1}(v_a)$ decreases slowly towards E_L, whereas $-H_{A2}(v_a)$ and $-H_{A3}(v_a)$ rapidly decrease and asymptotically approach E_L. It seems that $H_{A1}(v_a)$ represents the change of H_A in the process of packing the first layer, $H_{A3}(v_a)$ in the formation of the higher layers and $H_{A2}(v_a)$ in the intermediate state. In Fig. 2 the full line gives the variation of H_A

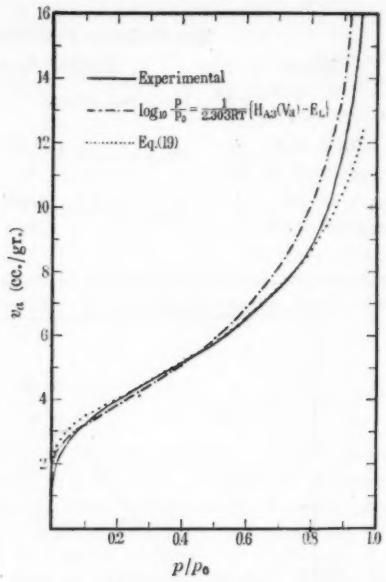


Fig. 4.—Adsorption Isotherm of Water on Anatatse at 25°C.

through the whole region in a smooth curve.

In Fig. 3 are presented the adsorption data[6] of water vapor on one gram of the anatase sample at 25°C. plotted according to the original authors. The straight line is obtained in the relative pressure range 0.3—0.7 (v_a varies in this region from 4.7 to 7.4 cc./gr.). We obtain as the H. J. isotherm in this case,

$$\log_{10}\frac{p}{p_0}=0.070-\frac{12.9}{v_a^2} \qquad (19)$$

while, inserting $H_{A2}(v_a)$ of (18) to (9), we get

$$\ln\frac{p}{p_0}=-\frac{\bar{S}(v_a)}{R}-\frac{1}{RT}\cdot\frac{14200}{v_a^2}$$

or

$$\log_{10}\frac{p}{p_0}=-\frac{\bar{S}(v_a)}{4.58}-\frac{10.4}{v_a^2} \qquad (20)$$

By comparing (19) and (20), it may be concluded that the general tendency of the adsorption is mainly determined by the enthalpy part of the isotherm in the medium region of relative pressure. That the function $H_{A3}(v_a)$ is adopted instead of $H_{A1}(v_a)$ and $H_{A2}(v_a)$, is because it not only represents the actual enthalpy change in the medium the higher

(5) A. B. Lamb and A. S. Coolidge, *J. Am. Chem. Soc.*, **42**, 1146 (1920).

(6) W. D. Harkins and G. Jura, *J. Am. Chem. Soc.*, **66**, 1366 (1944).

pressure regions but also reflects the outline of the whole isothermal variation as shown in Fig. 4.

IV. The Harkins—Jura's Theory and the Constants in Their Isotherm

In the case of the water vapor—anatase system, it has been found that $H_A - E_L$ is inversely proportional to v_a^2 in the later stage of adsorption, and that it determines the outline of the isotherm. If it is admitted that these conclusions generally apply to the H. J. type isotherms, a reasonable solution to the questions raised at the beginning of this paper is obtained.

(i) Multimolecular Adsorption and H_A (v_a).—We have in general

$$\log_{10}\frac{p}{p_0} = -\frac{\bar{S}(v_a)}{2.303R} + \frac{1}{2.303RT}\{H_A(v_a) - E_L\} \quad (21)$$

According to the above viewpoint, we put

$$H_A(v_a) - E_L = -K_n/v_a^2 \quad (22)$$

where K_n is a constant.

Provided that the first term of the right-hand side of (21) is neglected, the fact that the H. J. isotherm contains the inverse square term of v_a is necessarily ascribed to the form of H_A (v_a) given by (22).

Eq. (22) suggests the picture on the potential field in the neighbourhood of the adsorbent surface, namely in the early stage of adsorption the molecules are settled in the deep potential near the surface, while as the adsorption proceeds the packing of the molecules is gradually extended to the place of flattened potential further from the surface and finally those occupying the furthest sites evolve only the heat of condensation. These situations are characteristic of the multimolecular adsorption, and are roughly reflected on the form of H_A (v_a) in Eq. (22). We may hence deduce the conclusion that this form of $H_A(v_a)$ and consequently the H. J. isotherm are peculiar to the multimolecular adsorption.

Generalizing Eq. (2), we have the following isotherm,

$$\log_{10}\frac{p}{p_0} = B - \frac{A}{v_a^n} \quad (23)$$

where n is a constant.

The second term of the right-hand side of (23) seems to be of an adequate form to represent the variation of the enthalpy part in the later stage of adsorption. On account of this the similar interpretations can be applied to this case.

(ii) The H. J. Constants and the "Relative Method".—As mentioned in Sec. II, the differential enthalpy is essentially the function of θ. Introducing v_m in place of N_0,

$$v_m = V\frac{N_0}{N}$$

Thus (22) is rewritten as

$$H_A(\theta) - E_L = -K_m(v_m/v_a)^2 \quad (24)$$

where K_m is the constant equal to K_n/v_m^2.

If we recall the preponderance of the enthalpy part in the medium pressure region, we put

$$\frac{A}{v_a^2} \approx \frac{1}{2.303RT}\{-H_A(\theta) + E_L\} \quad (25)$$

where A is the constant in Eq. (2).

As v_m is given by $V\ N_0/N$ or $V\Sigma/N\sigma_0$*, (24) and (25) give

$$A \approx \frac{K_m}{2.303RT}\frac{V^2\Sigma^2}{N^2\sigma_0^2} \quad (26)$$

Since Σ is naturally common for the same adsorbent, AT is expected to be proportional to K_m/σ_0^2, and $AT\sigma_0^2$ to K_m, provided that (25) is valid. It is seen from column 5 of Table 1 that the order of magnitude in AT is reverse to the size of molecule, i. e., water > nitrogen > n-butane > n-heptane. This is quite natural, so far as AT is inversely proportional to σ_0^2. In column 6 are shown the probable values of σ_0 at the temperatures listed in column 2. Eq. (24) indicates that K_m is the excess molar differential enthalpy at $v_a = v_m$, so that the polyatomic molecules or the molecules having large dipole moment should have great values of K_m. This is the same with $AT\sigma_0^2$, regarded as to be proportional to K_m. The result given in the last column is just as expected; the order in $AT\sigma_0^2$ is water > n-heptane > n-butane > nitrogen.

v_a in Eq. (2) remains definite at $p = p_0$ unless B is zero. In Fig. 4, however, the experimental curve increases towards infinity as p approaches p_0, though B is determined as 0,070 in this case. Hence it is to be noted that B is not always equal to the actual value of A/v_s^2.

* σ_0 is the area per molecule at $N_s = N_0$, given by Σ/N_0.

From the above point of view, it is possible to give a support to the "relative method". Provided that "heats of adsorption (of a vapor) seem to be roughly the same whether the adsorbent is charcoal, a metal or an oxide[7]", K_m is a peculiar constant to the vapor and independent of adsorbents, so that, roughly speaking, the constant k of (4) depends solely on the kind of vapors at a definite temperature. This is consistent with the original authors' viewpoint.

(iii) The Two-Dimensional Equation of State.—If the contributions of the entropy term to the free energy of the film is ignored according to the results in (i) and (ii), the work required to evaporate N_a adsorbed molecules into the vapor phase can be approximated by the energy of desorption of the film, q_a, in the medium pressure region.

From (24), we have

$$H_A(\theta) - E_L = -K_m(v_m/v_a)^2 = -K_m(N_0/N_A)^2$$

The corresponding h_2, which has the integrated form of H_A, is written as

$$-h_a = \frac{N_A}{N} E_L + k_2 - k_1 \frac{N_0^2}{N_A} \qquad (27)$$

where k_2 and k_1 are constants.

Thus q_a is given by

$$-q_a = \frac{N_A}{N} Q_L + k_2 - k_1 \frac{N_0^2}{N_A} \qquad (28)$$

where Q_L is the molar heat of condensation. Provided that the right-hand side of (27) or (28) is composed of a power series of N_0^n/N_A^{n-1}, we can put

$$k_2 = k_3 N_0$$

where k_3 is a constant.

Hence we obtain

$$-F_a \approx \frac{Q_L}{N} N_A + k_3 N_0 - k_1 \frac{N_0^2}{N_A} \qquad (29)$$

Substituting (29) into (12), we reach the equation of state from which Harkins and Jura started,

$$\pi \approx b - a\sigma$$

with

$$b = k_3/\sigma_0$$
$$a = 2k_1/\sigma_0^2.$$

(7) S. Brunauer, "The adsorption of Gases and Vapors", Vol. I. p 240, Princeton University Press, Princeton, N. J. (1945).

V. Acknowledgement

The author is grateful to Prof. Isamu Sano of this Institute for his interest and encouragement. He is also indebted to Dr. Yutaka Miyahara of this Instisute, to Dr. Keizo Suzuki of Gifu University, and to Dr. Yuzuru Ôshika of Kobayashi Institute of Physical Research, for their helpful advice. The cost of this research has been defrayed from the Scientific Research Grant of the Ministry of Education.

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Equilibrium of the CO_2-NH_3-Urea-H_2O System under High Temperature and Pressure. III. Effect of Water Added on Liquid-Vapor Equilibrium

By Schôhachi KAWASUMI

(Received August 28, 1952)

It was found by Fichter and Becker[1] experimentally in 1911 that the initial presence of water has a strongly depressing influence on the conversion of ammonium carbamate to urea. This fact was later substantiated by several investigators. To date no one, however, has satisfactorily shown the effect of water added to ammonium carbamate on the liquid-vapor equilibrium of the system. The present paper covers a study of the variation

(1) Fichter and Becker, *Ber.*, **44**, 3473 (1911).

of the equilibrium pressure, the liquid and vapor compositions and densities with an increase in the amount of water in the original charge.

Measurements were begun after heating the system at 160°C. for 20 to 24 hours. Since the equilibrium of the system is dependent on the weight of the carbamate in a given reaction volume as reported in the previous paper,[2],[3], experiments were conducted in which the initial loading density of ammonium carbamate (D) was 0.60 g./cc. Mole ratio of water added to ammonium carbamate (W) was varied from 0.20 to 1.00. Consequently the total loading density including water added is over 0.60 g./cc.

Experimental Results and Discussion

Equilibrium Pressure: Results of investigation of the effect of water added on the equilibrium pressure which was measured from the carbamate side of the reaction and also from the urea and water side by means of an apparatus reported in the previous paper[2] are shown graphically in Fig. 1. The figure shows the equilibrium pressure

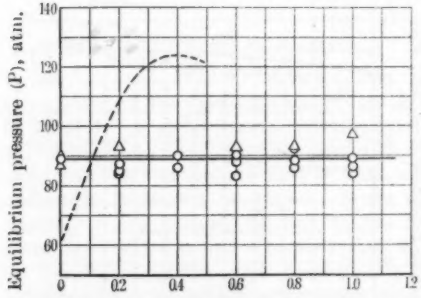

Fig. 1.—Effect of water added to ammonium carbamate on the equilibrium pressure

Curve	Investigator	Temp. °C.	Initial Content
----	Krase and Gaddy[4]	150	Carbamate and Water
——	Present Measurement at D=0.60 g./cc.	160	○ Urea and Water △ Carbamate and Water

to be approximately constant independent of mole ratio of water added to ammonium carbamate and of the kinds of starting materials within the experimental error. Only a study of the effect of water on the equilibrium pressure has been performed by N. W. Krase and V. L. Gaddy.[4] They showed that an increase in the percentage of water is accompanied by an increase in the total pressure of the charge as shown in Fig. 1, and gave a possible explanation that it is because of an increase in partial pressure of carbon dioxide as an increased percentage of ammonia was removed from the vapor phase on account of its greater solubility in water with increasing amount of water added. It is impossible to criticize their experiments since they made no reference to the apparatus and method of pressure measurement. Accordingly, the discrepancy between the two experimental results is obscure.

Vapor- and Liquid-Compositions: The effects of water added to the system on mole ratios (R' and S') of ammonia and water, respectively, to carbon dioxide in the vapor phase and on mole ratio (R) of unconverted ammonia to carbon dioxide in the liquid phase, measured by the methods reported in the previous paper,[3] are shown in Fig. 2 and 3 respectively. Both the

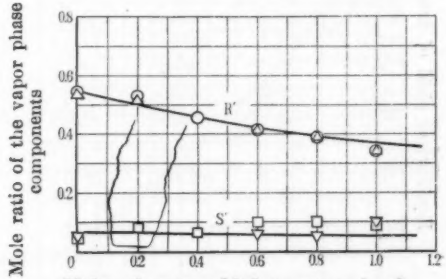

Fig. 2.—Effect of water added to ammonium carbamate on the vapor composition at 160°C. and D=0.60 g./cc.

Symbol	Initial Content	Mole Ratio
○	Urea and Water	Ammonia to Carbon Dioxide (R')
△	Carbamate and Water	
□	Urea and Water	Water to Carbon Dioxide (S')
▽	Carbamate and Water	

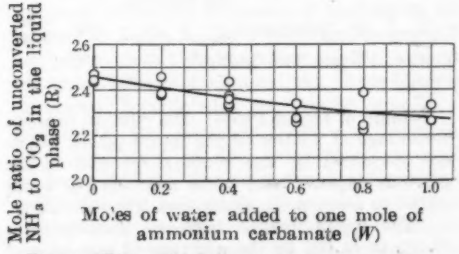

Fig. 3.—Effect of water added to ammonium carbamate on the liquid composition at 160°C. and D=0.60 g./cc.

(2) S. Kawasumi, This Bulletin, **24**, 148 (1951).
(3) S. Kawasumi, ibid., **25**, 227 (1952).
(4) N. W. Krase and V. L. Gaddy, *J. Ind. Eng. Chem.*, **14**, 611 (1922).

vapor- and the liquid-compositions become richer in carbon dioxide with the increase of mole ratio (W) of water added to ammonium carbamate, and mole ratio (S') of water to carbon dioxide in the vapor phase is approximately constant independent of the amount of water added.

Equilibrium Yield of Urea: It is evident that added water causes the equilibrium yield of urea to fall off, so that the best yield is obtained with pure ammonium carbamate. The results of the present study of the relation between the equilibrium yield of urea (Y) and mole ratio (W) of water added to ammonium carbamate are shown in Fig. 4 together with the results of other investigators.[4],[5],[6]

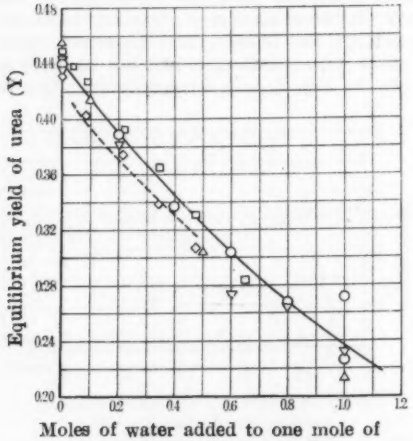

Fig. 4.—Effect of water added to ammonium carbamate on the equilibrium yield of urea

Symbol	Investigator	Initial content	Temp., °C.	D, g./cc.
—○— } —▽—	Present measurement	Urea and water Carbamate and water	160	0.60
△	Kitawaki, Hori and Shimoda[6]		160	0.65
◇ } □	M. Tokuoka[5]		150	0.50 0.90
------	Krase and Gaddy[4]		150	—

Volume of Liquid Phase: The relation between percentage of volume of the liquid phase, which was measured by the method reported in the previous paper,[3] and mole ratio (W) of water added to ammonium carbamate is shown in Fig. 5. The liquid volume increases linearly from 48.0% to 61.0% by the addition of one mole of water to one mole of ammonium carbamate.

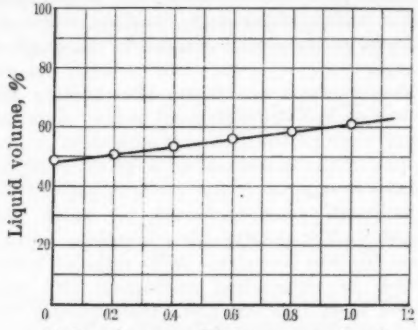

Fig. 5.—Relation between liquid volume and water added at 160°C. and $D=0.60$ g./cc.

Effect of Water on Liquid-Vapor Equilibrium Compositions

The liquid-vapor equilibrium compositions at 160°C. and $D=0.60$ g./cc., which were calculated from the above-mentioned data on the same assumption and by the same method

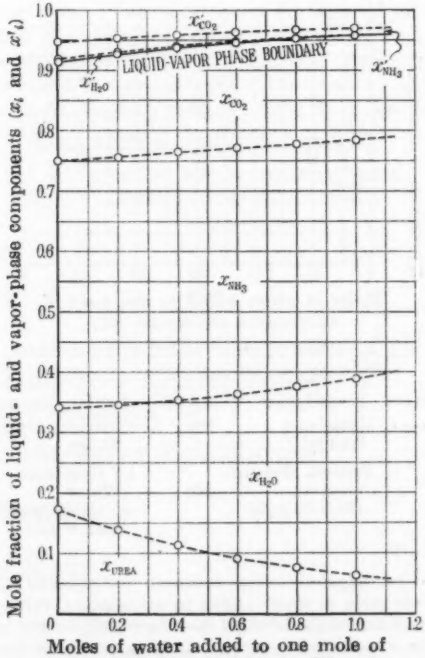

Fig. 6.—Liquid-vapor equilibria diagram of the CO_2-NH_3-Urea-H_2O system in the presence of water added.
(Temp.=160°C. and $D=0.60$ g./cc.)

(5) M. Tokuoka, *J. Agr. Chem. Soc. Japan*, **10**, 1333 (1934), ibid. **11**, 107 (1935), ibid. **11**, 174 (1935).
(6) Kitawaki, Hori and Shimoda, *Bull. Gov. Chem. Ind. Res. Inst. Tokyo*, **32**, No. 6 and 10 (1937).

Table 1

Effect of Water Added to Ammonium Carbamate on Liquid and Vapor Phase Compositions in Equilibrium State at 160°C. and D=0.60 g./cc. (c=7.685 mole/l.)

W, mole water/mole carbamate			0	0.20	0.40	0.60	0.80	1.00
P, atm.			89	89	89	89	89	89
R'			0.547	0.500	0.460	0.425	0.395	0.370
S'			0.066	0.062	0.060	0.057	0.056	0.054
R			2.460	2.410	2.365	2.330	2.300	2.275
Y			0.442	0.390	0.345	0.304	0.268	0.237
Equilibrium Concentration,	mole/l.	n'_{CO_2}	1.031	1.006	0.964	0.927	0.886	0.847
		n'_{NH_3}	0.564	0.503	0.444	0.394	0.350	0.313
		n'_{H_2O}	0.068	0.062	0.058	0.053	0.050	0.046
		n_{CO_2}	3.257	3.682	4.070	4.422	4.740	5.016
		n_{NH_3}	8.012	8.873	9.624	10.304	10.902	11.413
		n_{Urea}	3.397	2.997	2.651	2.336	2.059	1.822
		n_{H_2O}	3.329	4.472	5.667	6.894	8.157	9.461
	mole fraction	N'_{CO_2}	0.620	0.640	0.658	0.674	0.690	0.702
		N'_{NH_3}	0.339	0.320	0.303	0.287	0.272	0.260
		N'_{H_2O}	0.041	0.040	0.039	0.039	0.038	0.038
		N_{CO_2}	0.181	0.184	0.185	0.185	0.183	0.181
		N_{NH_3}	0.445	0.443	0.437	0.430	0.422	0.412
		N_{Urea}	0.189	0.150	0.120	0.097	0.080	0.066
		N_{H_2O}	0.185	0.223	0.258	0.288	0.315	0.341
d', g./cc.			0.109	0.109	0.108	0.110	0.110	0.111
d, g./cc.			1.131	1.133	1.139	1.132	1.135	1.139
K_{N_1}			0.974	0.926	0.876	0.817	0.773	0.733

as reported in the previous paper,[3] are shown in Table 1. A plot of mole fraction (x_i and x'_i) of components in the two phases against mole ratio (W) of water added to ammonium carbamate is drawn in Fig. 6. From these results, it has become evident that a large percentage of water added to the system exists in the liquid phase, and consequently the volume of the liquid phase increases with an increase of the amount of water added. It may be concluded that the constancy of the equilibrium pressure independent of the amount of water added to the system is because of a decrease in total mole of components in the vapor phase on account of their greater solubility in water as well as of a decrease in the volume of the vapor phase with an increase of the amount of water added.

The equilibrium constants K_{N_1} of the following reaction represented by mole fraction N_i

$$CO_2+2NH_3 \rightleftarrows CO(NH_2)_2+H_2O \qquad (1)$$

$$K_{N_1}=\frac{N_{Urea}N_{H_2O}}{N_{CO_2}N^2_{NH_3}}$$

are shown in the last line of Table 1. As the values of K_{N_1} show a tendency to decrease gradually with an increase of water added to the system at a given temperature, K_{N_1} is not an equilibrium constant in the true sense of the term. The equilibrium constant should be calculated on the other assumption and discussed from the other stand-point.

Liquid- and Vapor-Density

Results of calculation of the liquid- and vapor-density (d and d') at 160°C. and over the range of mole ratio (W) from 0.20 to 1.00 of water added to ammonium carbamate are shown in Table 1. Both densities are approximately constant independent of the amount of water added. In general, the vapor-density increases linearly with the rise of pressure as shown in the previous paper.[3] Therefore, the constancy of the equilibrium pressure independent of the amount of water added will also be reasonable from the results of calculation of the vapor-density, since it undergoes little change by the addition of water.

Summary

(1) The effect of water added to ammonium

carbamate on liquid-vapor equilibrium of the CO_2-NH_3-Urea-H_2O system was investigated at 160°C. and a loading density of ammonium carbamate 0.60 g./cc. and over the range of mole ratio from 0.20 to 1.00 of water added to ammonium carbamate.

(2) The equilibrium pressure is approximately constant independent of the amount of water added within the range of the experimental conditions. Both the vapor- and the liquid-compositions become richer in carbon dioxide, and the equilibrium yield of urea decreases with an increase of the amount of water added.

(3) The results of calculation of the compositions and densities of the liquid- and the vapor-phases in the equilibrium state when water ranging from 0.20 to 1.00 mole was added to one mole of ammonium carbamate have been shown.

Research Department, Niihama Works, Nissin Chemical Co., Ltd., Niihama.

Equilibrium of the CO_2-NH_3-Urea-H_2O System under High Temperature and Pressure. IV. Effect of Loading NH_3-CO_2 Mole Ratio on Equilibrium Pressure and Vapor Composition

By Schôhachi KAWASUMI

(Received August 28, 1952)

In 1918 Fichter, Steiger and Stanisch[1] found ammonia to exert a beneficial influence for the formation of urea from ammonium carbamate only when moderate amounts were used in their experiment in which they heated ammonium carbamate with ammonia. H. J. Krase and V. L. Gaddy[2] later obtained the yield of urea of 80 to 85% calculated on ammonium carbamate initially charged in the presence of as much as 300% excess ammonia at a temperature of 155°C. They explained that an excess amount of ammonia over that combined as carbamate acts as a dehydrating agent, removing the water from the active mass, thus preventing its reaction with urea and thereby shifting the equilibrium toward the urea side. They found also that an excess amount of carbon dioxide added to carbamate exerts no such effect. In the same way, Hori and Ogami[3] investigated the yield of urea in the presence of excess ammonia over the temperature range from 130° to 180°C. and found excellent agreement with the mass law according to the equation:

$$CO_2+2NH_3 \rightleftharpoons CO(NH_2)_2+H_2O \quad (1)$$

However, the equilibrium constant of the equation (1) employed by them was represented by mole fraction derived from the initial loading composition and the yield of urea without distinction between the liquid- and vapor-compositions. It is evident that the liquid-vapor phase equilibrium of the system is dependent upon the loading density of the initial content in the reaction vessel in the presence of excess ammonia or carbon dioxide as well as in the stoichiometrical loading mole ratio of $2NH_3$ to $1CO_2$.[4]

No one, to my knowledge, has shown the effect of excess ammonia or carbon dioxide added to ammonium carbamate on the liquid and vapor phase equilibrium. The effects of the variation of the loading mole ratio of ammonia to carbon dioxide over the range from 1.60 to 3.40 on the equilibrium pressure and the composition of the vapor phase are described in this paper.

Experimental Procedure

The equilibrium pressure and the composition of the vapor phase were respectively determined

(1) Fichter, Steiger and Stanisch, *Verhandl. Naturforsch. Ges. Basel*, **28**, II, 66 (1918); *Chem. Abst.*, **14**, 540 (1920).

(2) H. J. Krase and V. L. Gaddy, *J. Am. Chem. Soc.*, **52**, 3088 (1930).

(3) Hori and Ogami, *J. Soc. High Pressure Gas Ind. Japan*, **6**, 256 (1942).

(4) S. Kawasumi, This Bulletin, **24**, 148 (1951).

with the methods reported in the previous papers[4][5] after heating the reaction vessel at 160°C. for 20 to 24 hours. The starting materials were prepared by loading ammonium carbamate or equi-molar urea and water into the reaction vessel with a constant loading density of 0.60 g./cc., followed by the addition of the required amounts of liquid ammonia or solid carbon dioxide to it by the procedure described below. Consequently, the total loading density including excess liquid ammonia or solid carbon dioxide was more than 0.60 g./cc. The amount of liquid ammonia and solid carbon dioxide added to one mole of carbamate ranged from 0.10 to 1.40 moles and from 0.10 to 0.25 moles, respectively. In other words, the range of the loading mole ratio of ammonia to carbon dioxide covered in the present study was 1.60 to 3.40.

Procedure for Loading Liquid Ammonia:—Loading of excess liquid ammonia was accomplished by a special method measuring its weight directly without such a steel weighing pipette as employed by Krase and Gaddy,[2] or steel bomb equipped with a liquid level indicator in order to measure its volume as usually employed. Ammonium carbamate or equi-molar urea and water was weighed out accurately in a glass beaker, as large as the reaction vessel can hold as shown in Fig. 1, which was put on the left pan

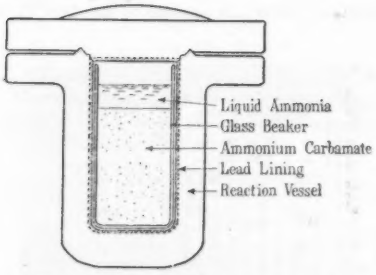

Fig. 1.—Experimental apparatus.

of the balance. After the balance weight equivalent to the required amount of liquid ammonia to be added to carbamate was put on the right pan, liquid ammonia withdrawn previously from its bomb in an open vessel was poured on the above content in the glass beaker on the left pan. Since the vaporisation of ammonia initially charged induces the cooling of the glass beaker and its content due to the latent heat of the vaporisation, it is possible to charge a required amount of liquid ammonia, accurately, into the beaker. This mixture was introduced into the reaction vessel together with the beaker, and then the vessel was closed as quickly and securely as possible, to prevent the loss of material by leakage. If the procedure was finished within a few minutes, only a negligibly small quantity of gaseous ammonia was lost during the above manipulation.

Procedure for Loading Solid Carbon Dioxide:—A required quantity of solid carbon dioxide was weighed out and then as soon as it was introduced into the reaction vessel in which ammonium carbamate was previously charged, the reaction vessel was closed as quickly as possible.

Experimental Results and Discussion

Relation between Equilibrium Pressure and Loading Composition:—The effect of the loading mole ratio of ammonia to carbon dioxide (L) on the equilibrium pressure (P) has been investigated at a temperature of 160°C. from several starting materials, which were prepared by adding liquid ammonia or solid carbon dioxide respectively to ammonium carbamate only, an equi-molar mixture of urea and water, or an equi-molar mixture of carbamate, urea and water which were loaded at a constant density of 0.60 g./cc. in each case.

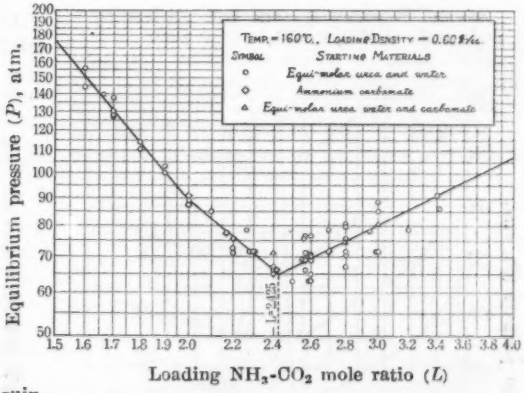

Fig. 2.—Equilibrium pressure of the CO_2-NH_3-Urea-H_2O system in the presence of excess ammonia or carbon dioxide at 160°C.

The results of these experiments are shown by three straight lines as a plot of the logarithm of P against the logarithm of L in Fig. 2. The equilibrium pressure rises up with increasing the excess amount of carbon dioxide and it reaches 150 atmospheres at a loading mole ratio $L=1.60$. No one, to my knowledge, has shown the relation between P and L, and yet it has usually been conjectured that the same pressure rise may be observed with increasing the excess amount of ammonia.

(5) S. Kawasumi, This Bulletin, **25**, 227 (1952).

Dr. S. Kodama,[6] Professor of Kyoto University, however, suggested three years ago that the equilibrium pressure had a tendency to decrease with excess ammonia, when it was added to ammonium carbamate, to the minimum. The present measurements at 160°C. have also shown the system definitely to exert the minimum pressure at a loading mole ratio $L=2.43$. The reason why the minimum pressure is caused by the addition of excess ammonia is explained in the following section. The results of these experiments are represented by three empirical equations as shown in Table 1. A discontinuous point at a loading mole ratio of $2NH_3$ to $1CO_2$, where only carbamate or equi-molar urea and water were initially loaded in the reaction vessel, may possibly be attributed to the fact that the total loading density is minimum at this point.

Table 1

Empirical Equations for the Equilibrium Pressure of the CO_2-NH_3-Urea-H_2O System in the Presence of Excess Ammonia or Carbon Dioxide at 160°C. and $D=0.60$ g./cc.

Range of L	Empirical Equation
1.60—2.00	$P=459.5\,L^{-2.372}$
2.00—2.43	$P=273.4\,L^{-1.618}$
2.43—3.40	$P=26.75\,L$

where P= pressure, atm. and L= loading mole ratio of NH_3 to CO_2

Relations between the equilibrium pressure and the loading composition over the temperature range from 130° to 190°C. are shown in Fig. 3. These experiments were performed with the initial mixtures of equi-molar urea and water and excess ammonia. The loading mole ratio of ammonia to carbon dioxide at which the system exerts the minimum equilibrium pressure varies from 2.4 to 2.5 with the rise of temperature from 130° to 190°C. as indicated by a broken line in Fig. 3.

Relation between Vapor Composition and Loading Composition :—Mole ratios of ammonia to carbon dioxide (R') and of water to carbon dioxide (S') in the vapor phase in the equilibrium with the liquid phase have been determined at a temperature of 160°C. and over the range of the loading mole ratio $L=1.60$ to 3.40. A plot of the logarithm of the measured mole ratios of R' and S' against the logarithm of L is respectively shown in Fig. 4, in which $R'-L$ relation at 160°C. is represented by the following equation.

$$R'=L^{6.764}/2\times10^3.$$

At $L=2.43$ where the system exerts the minimum equilibrium pressure at 160°C. as

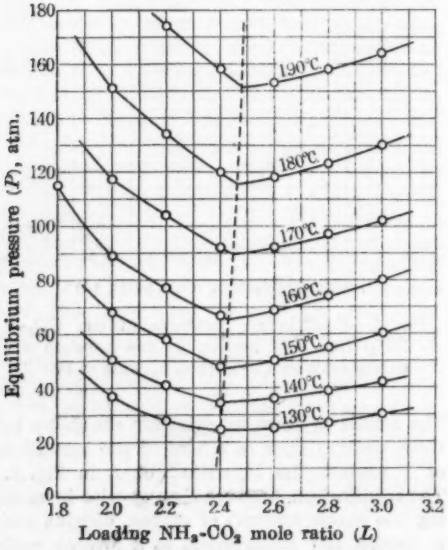

Fig. 3.—P-L-T relations of the CO_2-NH_3-Urea-H_2O system

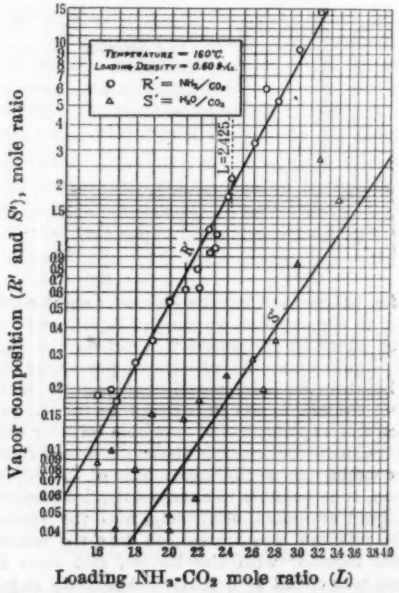

Fig. 4.—Vapor composition of the CO_2-NH_3-Urea-H_2O system in the presence of excess ammonia or carbon dioxide at 160°C.

(6) S. Kodama, *Unpublished report at Research Department, Nissin Chem. Co.* (1950).

pointed out in the preceding section, definitely $R'=2.00$, that is to say, the mole ratio of ammonia to carbon dioxide in the vapor phase is equivalent to the composition of ammonium carbamate.

Relation between Vapor Cmposition and Equilibrium Pressure :—For the purpose of studying the relation between the vapor composition and the equilibrium pressure, the partial pressures of each of the components (p_{CO_2}, p_{NH_3} and p_{H_2O}) in the vapor phase under several conditions have been calculated from the previous investigations of the author[4],[5] assuming the vapor to be a perfect gas. Table 2~4 show respectively the variations of the partial pressure with the temperature at a constant loading density (D) of 0.60 g./cc., the variation with the loading density of ammonium carbamate in the absence of excess ammonia or carbon dioxide, and the variation with the amount of water added to one mole of carbamate (W) at a constant temperature of 160°C. Table 5 shows the results of calculation from the present measurement of the vapor compositions under the conditions of $L=1.6-3.0$, $D=0.60$ g./cc. and 160°C.

According to trial calculations of $K_p=p_{CO_2}p^2_{NH_3}p_{H_2O}$ which are shown in these Tables, the logarithm of K_p is a linear function of the temperature over the range between 140° and 180°C. as shown in Fig. 5, while at a constant temperature of 160°C. $K_p\times10^{-5}$ is

Table 2

Relation between Partial Pressure of the CO_2-NH_3-Urea-H_2O System and Temperature at Constant Loading Mole Ratio $L=2.00$ and Loading Density of 0.60 g./cc.

Temp., °C.	Partial Pressure, atm. p_{CO_2}	p_{NH_3}	p_{H_2O}	$K_p\times10^{-5}$
140	33.4	15.7	1.4	0.115
150	43.7	22.0	2.3	0.486
160	55.2	30.2	3.6	1.81
170	69.9	41.4	5.7	6.83
180	86.1	55.9	9.0	24.2

Table 3

Relation between Partial Pressure of the CO_2-NH_3-Urea-H_2O System and Loading Density at Constant Temp.=160°C. and Loading Mole Ratio $L=2.00$

D, g./cc.	Partial Pressure, atm. p_{CO_2}	p_{NH_3}	p_{H_2O}	$K_p\times10^{-5}$
0.20	27.2	37.0	4.5	1.70
0.40	39.9	32.5	4.1	1.73
0.60	55.2	30.2	3.6	1.81
0.80	74.2	30.0	3.3	2.20
1.00	100.6	32.6	3.3	3.53

Table 4

Relation between Partial Pressure of the CO_2-NH_3-Urea-H_2O System and Added Water at Constant Temp.=160°C., Loading Mole Ratio $L=2.00$, and Loading Density $D=0.60$ g./cc.

Added water, mole/mole, carbamate	Partial Pressure, atm. p_{CO_2}	p_{NH_3}	p_{H_2O}	$K_p\times10^{-5}$
0	55.2	30.2	3.6	1.81
0.20	57.0	28.5	3.5	1.62
0.40	58.5	27.0	3.5	1.49
0.60	60.0	25.6	3.4	1.34
0.80	61.3	24.2	3.5	1.26
1.00	62.5	23.1	3.4	1.13

Table 5

Relation between Partial Pressure of the CO_2-NH_3-Urea-H_2O System and Loading Mole Ratio at Constant Temp.=160°C. and Loading Density $D=0.60$ g./cc.

L, Loading mole ratio	Partial Pressure, atm. p_{CO_2}	p_{NH_3}	p_{H_2O}	$K_p\times10^{-5}$
1.60	127.9	19.9	3.2	1.62
1.80	86.0	24.6	3.4	1.77
2.00	55.2	30.2	3.6	1.81
2.20	35.4	36.7	3.9	1.86
2.40	21.8	40.4	3.8	1.35
2.62	15.0	50.6	3.9	1.50
2.80	11.2	59.6	4.2	1.67
3.00	7.4	68.4	4.2	1.46

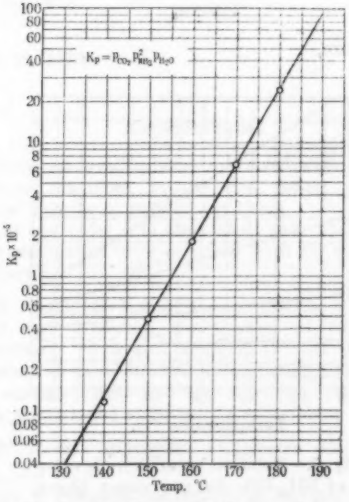

Fig. 5.—K_p-Temp. relation at $L=2$ and $D=0.60$ g./cc.

approximately constant (1.1～3.5) independent of D, W and L within the range of the present experimental conditions.

The approximate constancy of K_p seems to show that at least for practical purposes the assumption, that the activity of ammonium carbonate in the liquid phase is 1, is allowable. If we take such assumption as ammonium carbonate dissociates according to the equation:

$$(NH_4)_2CO_3(l) \rightleftharpoons CO_2(g)+2NH_3(g)+H_2O(g),$$

the equilibrium constant must be constant as follows.

$$K_p = P^4 N'_{CO_2} N'^2_{NH_3} N'_{H_2O} \equiv \text{a constant at } 160°C.$$

where P is the total pressure of the system and N_i' is the mole fraction of i-component in the vapor phase.

$$N'_{CO_2}+N'_{NH_3}+N'_{H_2O}=1$$

Accordingly,

$$K_p = P^4 N'^2_{NH_3}\{1-(N'_{NH_3}-N'_{H_2O})\}N'_{H_2O}$$

Supposing that N'_{H_2O} is constant,

$$\frac{\partial P}{\partial N'_{NH_3}} = \frac{K_p^{1/4}(3N'_{NH_3}+2N'_{H_2O}-2)}{4N'^{3/2}_{NH_3} N'^{1/4}_{H_2O}(1-N'_{NH_3}-N'_{H_2O})^{5/4}}$$

At a vapor composition where the system exerts the minimum pressure,

$$\frac{\partial P}{\partial N'_{NH_3}} = 0$$

Therefore,

$$3N'_{NH_3}+2N'_{H_2O}-2=0$$

or

$$R' \equiv \frac{N'_{NH_3}}{N'_{CO_2}} = 2$$

Thus, it has been verified that the mole ratio of ammonia to carbon dioxide in the vapor phase under the minimum pressure of the system at a given temperature is equal to that of ammonium carbamate independent of the amount of water in the vapor.

Effect of Temperature on Relation between Vapor- and Loading Composition: —Mole ratio of ammonia to carbon dioxide in the vapor phase (R') has also been determined at 140° and 180°C. as well as 160°C. over the range of the loading mole ratio L= 2.0—3.0.

The experimental results and empirical equations for $R'-L$ relations are given in Fig. 6. These three straight lines intersect at a

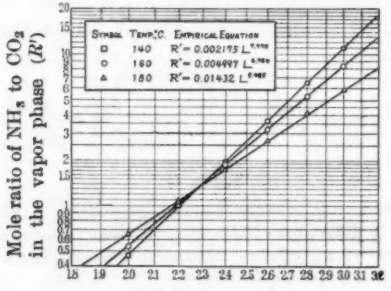
Symbol Temp.°C. Empirical Equation
□ 140 R'= 0.002175 L^3.778
○ 160 R'= 0.004697 L^3.765
△ 180 R'= 0.014432 L^3.667
Mole ratio of NH3 to CO2 in the vapor phase (R')
Loading NH3-CO2 mole ratio (L)

Fig. 6.—R'-L relations at 140°, 160° and 180°C.

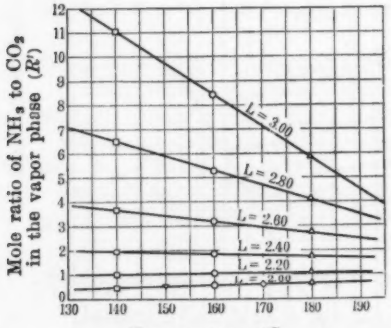

Fig. 7.—Relation between mole ratio of NH_3-CO_2 in the vapor phase and temperature over the range of L=2～3

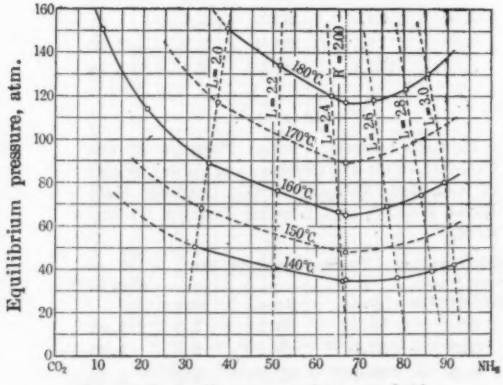

Fig. 8.—Equilibrium pressure-vapor composition diagrams for the CO_2-NH_3-Urea-H_2O system

point near $L=2.28$, where R' is constant independent of temperature. R' is also a linear function of temperature at a given loading composition as shown in Fig. 7.

From the above data, such a relation as shown in Fig. 8 is derived between the equilibrium pressure and ratio of ammonia to carbon dioxide in the vapor phase over the temperature range from 140° to 180°C. With a rise of temperature and a consequent increase of total pressure, the vapor composition becomes richer in ammonia at any loading composition less than $L=2.28$, while it becomes richer in carbon dioxide at more than $L=2.28$.

Summary

(1) For the purpose of studying the liquid-vapor equilibria of the CO_2-NH_3-Urea-H_2O system in the presence of excess ammonia and carbon dioxide respectively over that combined as ammonium carbamate, the equilibrium pressure and vapor composition of the system under high temperature and pressure have been determined over the range of the loading NH_3-CO_2 mole ratio from 1.60 to 3.00.

(2) The experiments which were performed with an initial loading density of ammonium carbamate into a reaction vessel of 0.60 g./cc. and at a temperature of 160°C. have definitely shown the system to exert the minimum pressure and simultaneously to have the vapor composition of $2NH_3$ to $1CO_2$ at a loading mole ratio of 2.43 NH_3 to $1CO_2$.

(3) The relation between the equilibrium pressure and the mole ratio of NH_3 to CO_2 in the vapor phase has been given diagrammatically over the temperature range from 140° to 180°C.

The writer wishes to express appreciation for the kind guidance and the advice received throughout this work from Dr. Shinjiro Kodama, Prof. of Kyoto University, and for the encouragement received from Dr. Kenji Fujimura, the chief of the Research Department.

Research Department, Niihama Works, Nissin Chemical Co., Ltd., Niihama

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Heats of Wetting of Polysaccharides. III. Heats of Wetting of Acetylated and Methylated Polysaccharides

By Toshio NAKAGAWA

(Received September 13, 1952)

Introduction

The origin of the heat developed when a polysaccharide is thrown into water, is generally ascribed to the interaction between the hydroxyl group of the substance and water molecule. But surprisingly, few experimental facts supporting this opinion have been reported. If this supposition is correct, the heat of wetting of a polysaccharide whose hydroxyl groups are substituted with less hydrophilic groups will become smaller than that of the mother substance.

The author measured the heats of wetting of acetylated starch, glycogen, inulin and konjacmannan, also that of methylated inulin, and obtained smaller values than those of their respective mother substances.

Experimental

Heats of wetting were measured with the apparatus described in the first report of this series[1] under evacuated condition.

The samples of acetylated and methylated polysaccharides were prepared with the following methods.

(1) **Acetylated starch.**—Acetylation was carried out following the method of Kerr and Cleveland[2] who had acetylated limit dextrin. Potato starch, which had been washed thoroughly by methanol with Soxhlet's extractor, was ground to a powder and subjected to acetylation.

(2) **Acetyl glycogen.**— Glycogen purified as

(1) T. Nakagawa, This Bulletin, **25**, 169 (1952).
(2) R. W. Kerr and F. C. Cleveland, *J. Am. Chem. Soc.*, **71**, 3455 (1949).

described in the first report,[1] was acetylated with a similar method.

(3) **Acetyl inulin.**—Powdered inulin (β form) was treated as reported by W. N. Haworth, E. L. Hirst and E. G. V. Percival.[3] The acetylated substance was purified by recrystallization from methanol.

(4) **Acetyl konjacmannan.**—From the preliminary examination, it became clear that β-konjacmannan is not suitable as a starting substance, so the acetylation was performed with α-konjacmannan.

Acetyl determinations were carried out by the method described by W. N. Haworth et al[4] and the result was as follows:

acetyl starch	43.5 %
acetyl glycogen	—
acetyl inulin	45.0 %
acetyl konjacmannan	44.8 %

(5) **Methyl inulin.**—Methyl inulin was obtained by the simultaneous deacetylation and methylation of acetyl inulin.[3]

The above-mentioned five samples were subjected to heat measurements after drying in Abderhalden's desiccator under 2/100 mm. Hg at 65°C.

(3) W. N. Haworth, E. L. Hirst and E. G. V. Percival, *J. Chem. Soc.*, 2384 (1932).
(4) W. N. Haworth and H. R. L. Streight, *Helv. chim. Acta.*, **15**, 609 (1932).

Results and Discussion

The heats of wetting of the above-mentioned substances are arranged in Table 1. in comparison with those of their mother substances.

Table 1

cal./g.

Acetyl starch	5.4	Starch (native)	28.2
		Starch (pasted)	24.6
		Starch (retrograded)	25.6
Acetyl glycogen	3.1	Glycogen	23.5
Acetylkonjacmannan	6.5	Konjacmannan (α)	23.7
		Konjacmannan (β)	16.2
Acetyl inulin	0.3	Inulin (β)	23.1
Methyl inulin	1.3	Inulin (α)	17.9
		Inulin (retrograded)	21.2

We see that the acetylated and methylated polysaccharides have much lower values than their mother substances. This fact may give a strong support to the opinion that the heats of wetting of polysaccharides are mainly attributed to the interaction between the hydroxyl groups and water.

The author wishes to express his sincere thanks to Prof. Sameshima for his kind guidance and encouragement.

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Sedimentation Volume of Alginic Acid Powder in Electrolyte Solution

By Shigeru MIYAMOTO and Tunetaka SASAKI

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Although there have been many studies on alginic acid and its salts, few studies have been carried out on the properties of alginic acid powder as a dispersed phase. In the present paper, it was attempted to study the colloid chemical properties such as sedimentation volume, degree of swelling, electrokinetic potential and cation exchange capacity of alginic acid powder in electrolyte solution.

Experimental

Alginic acid powder was prepared as follows. Alginic acid was precipitated from sodium alginate solution (polymerization degree being about 198) by adding hydrochloric acid, washed, and it was then dissolved in sodium carbonate solution. This procedure was repeated three times, after which alginic acid was precipitated, washed with water, methanol and ether, and then dried at 50°C for five hours. Dry alginic acid was ground in an agate mortar and the portion of 200~280 mesh was taken and kept in a glass bottle. The size and shape of particles were such that their longer axis was between about 0.02 and 0.1 mm. and the ratio of longer to shorter axis was less than about 1.4. The ash content of the sample was about 0.2 %. Electrolytes used were also purified by the usual method.

Sedimentation Volume.—10 cc. of an electrolyte solution was pipetted in a flat bottom glass tube of 1cm. inner diameter and 19 cm. height. 0.3 g of alginic acid powder was then added and the tube was shaken vigorously. The sedimentation volume reached a constant value after 3~7 days which was recorded as an equilibrium value.

Swelling Degree.—Sedimentation volume is considered to increase with increasing degree of coagulation[1],[2],[3],[4] as well as the swelling of the powder. Assuming that the sedimentation volume is proportional to the swollen volume when the coagulation degree does not change, the following relation is obtained.

$$S=(V_w \cdot X/X_w-v_w)/v_w \qquad (1)$$

Here, S is the swelling degree of alginic acid, V_w the sedimentation volume in water, X_w and X the swollen volume in water and in an electrolyte solution respectively, all referred to one gram of dry alginic acid. The quantity v_w is an apparent volume per gram of dry powder under the same degree of coagulation as in water. X and v_w are calculated by the following relations.

$$X=\{U-(W-p \cdot w_0)/d\}/p \qquad (2)$$

$$v_w=V_w/X_w \cdot \rho \qquad (3)$$

Here, U and W are the volume and weight of electrolyte solution with swollen alginic acid containing p gram of dry acid, respectively, w_0 the weight of swollen alginic acid per gram of dry substance, and d and ρ, densities of electrolyte solution and dry alginic acid, respectively. Of these quantities, w_0 was obtained by the measurement, in dry and swollen state, of the weights of alginic acid film prepared on a microscopic slide.

Coagulation Degree.—In general, the sedimentation volume increases with the increasing degree of coagulation. Assuming that swelling and coagulation contribute to the sedimentation volume additively, coagulation degree C is expressed as follows.

$$C=(V_E-V_w \cdot X/X_w)/v_w \qquad (4)$$

Here, V_E is the sedimentation volume in an electrolyte solution. The value of C in water was taken as the standard. From (1) and (4),

$$\Delta v \equiv S+C=(V_E-v_w)/v_w \qquad (5)$$

results, which means that the specific sedimentation volume Δv is the sum of the degrees of swelling and coagulation.

Electrokinetic Potential.—Cataphoretic velocity and ζ-potential of alginic acid were measured for particles suspended in various electrolyte solutions. Namely, a dilute suspension of alginic acid is introduced in U-tube and the sedimentation velocity u_1 is measured under a definite gradient of electrostatic field E. The field is reversed and the velocity u_2 is measured again. Then the following relation holds.

$$G+k\zeta E=au_1 \qquad (6a)$$

$$G-k\zeta E=au_2 \qquad (6b)$$

Here, G represents the force due to gravity and k and a, two constants. Then,

$$\zeta=a(u_1-u_2)/2k \cdot E \qquad (7)$$

gives ζ-potential when we use proper value for a/k[5].

Cation Exchange Amount.—Alginates formed by mixing alginic acid powder and the electrolyte solutions of varying concentration were washed and burnt in a crucible. Cation exchange amounts for the electrolytes of various concentrations were estimated from the amount of metal oxide formed. Values of pH of electrolyte solutions were 1.5~1.8 for cupric, aluminum and ferric chlorides.

Experimental Results

Preliminary experiments were carried out to study the effects of temperature, particle size and the redispersion upon the sedimentation volume as shown in Tables 1 and 2.

Table 1

Effects of temperature, particle size on sedimentation volume*

Temp. (°C.)	Particle Size (Mesh)	Sed. Vol. in 3N KCl Solution (cc./g.)
0	280<	7.9
10	〃	7.0
37	〃	5.9
10	〃	7.0
10	200~280	5.4
10	110~150	4.3
10	70~100	4.4

Table 2

Effect of redispersing the sediment on sedimentation volume*

Temp. (°C.)	Particle Size (Mesh)	Sed. Vol. (cc./g.) in 3N KCl after Repeated Disp.			
		0	1st	2nd	3rd
10	280<	7.9	6.2	5.9	5.8

The maximum error introduced in the sedimentation volume measurement was ±13% for

(1) P. Ehrenberg, "Bodenkolloide", p. 83, 84, Dresden (1918).
(2) A. v. Buzágh, *Kolloidchem. Beih.*, **32**, 114 (1931).
(3) G. F. Kandilaron, *Kolloid-Z.*, **90**, 320 (1940).
(4) W. Gallay and I. E. Puddington, *Can. J. Research*, **21 B**, 171 (1943); **22 B**, 16 (1944).
(5) H. A. Abramson, "Electrokinetic Phenomena", p. 111, Chem. Catalog, New York (1934).
* Alginic acid powder stored for about five months after purification was used.

thorium nitrate solution and about ±7% for most other cases. Values of sedimentation volume in various electrolyte solutions are shown in Fig. 1.* Values of *p*H of these solutions were 2.0~2.2

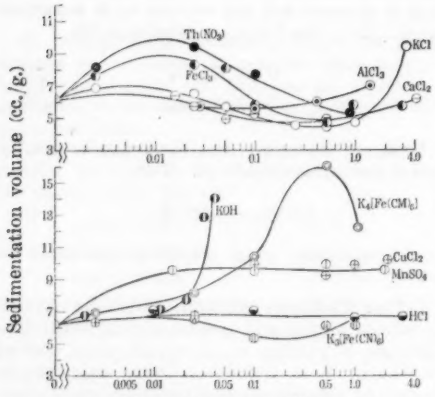

Fig. 1.—Sedimentation volume of alginic acid powder in various electrolyte solutions.

for potassium and calcium chlorides, 1.5~1.8 for cupric, aluminum and ferric chlorides and 1.7~1.9 for thorium nitrate. The effects of its change on the sedimentation volume proved to be negligible. We can see as a whole in this figure that the sedimentation volume exhibits a maximum at relatively low concentration of electrolyte and minimum in the region of larger concentration. The maximum is especially marked in the case of thorium and ferric salts. We should, however, note the anomalous case for potassium hydroxide and potassium ferrocyanide where the anomalies are due perhaps to a strong basicity and negative polyvalency. We then calculated the swelling degree *S* according to the equation (1) which was

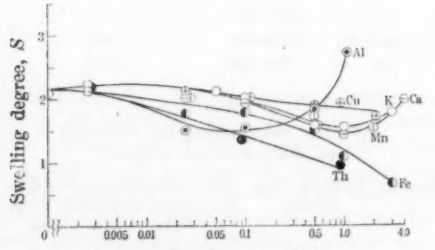

Fig. 2.—Values of swelling degree in various electrolyte solutions.

shown in Fig. 2. The swelling generally decreases

* Here a fresh sample of alginic acid was used.

with increasing concentration of electrolyte. It increases, however, at fairly large concentrations for some electrolytes. Further the coagulation degree *C* was shown in Fig. 3 a. In the cases of

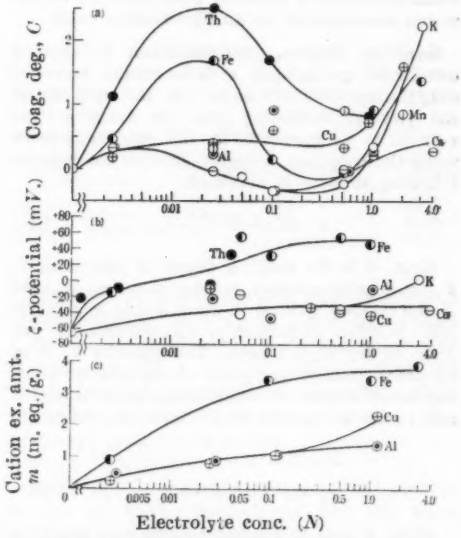

Fig. 3.—Coagulation degree, electrokinetic potential and cation exchange amount of alginic acid powder in various electrolyte solutions.

ferric chloride and thorium nitrate, the values of *C* showed a marked maximum at about 0.01 *N* of electrolyte concentration, while the rest of the salt gave rather a flat maxima at the same region of concentration. At higher concentration region, the values of *C* after passing a minimum tended to increase for all cases examined.

The electrokinetic potential was calculated using the equation (7), and shown in Fig. 3 b. For the calculation, a/k was equated to $4\pi\eta/D$, (η, being the viscosity coefficient and D the dielectric constant of water) according to the classical Helmholtz theory, since we were not interested here in the exact evaluation of a/k. It can be confirmed that the inversion of sign of ζ-potential takes place with increasing concentrations of electrolyte in the cases of ferric chloride and thorium nitrate and the isoelectric points of alginic acid particle correspond to the maxima of coagulation degree. Besides, the values of swelling degree *S* and coagulation degree *C* in various solutions of electrolytes with common cation or anion were measured and shown in Table 3. It seems that the differences of the effects of various electrolytes on coagulation degree are explained by the difference in amount of cation exchange adsorption which was shown in Fig. 3 c.

From this table, the following series of decreas-

ing order were obtained for anions (or cations) composing salt of common cation (or anion), with regard to the degrees of swelling and coagulation.

Table 3
Swelling and coagulation degrees in solutions of electrolytes with common cation or anion

Electrolyte	Conc. (N)	Sed.Vol. (cc./g.)	Swollen Wt., w	Swell. Deg., S	Coag. Deg., C
NH_4Cl	3.00	6.7	2.46	+1.08	+1.45
NaCl	3.00	6.8	2.56	+1.11	+1.47
KCl	3.00	9.4	2.93	+1.73	+2.22
$MgCl_2$	3.00	5.7	2.38	—	—
$CaCl_2$	3.00	5.6	2.51	—	—
$BaCl_2$	3.00	5.9	2.66	—	—
KCl	1.00	4.6	2.23	+1.52	−0.11
KBr	1.00	5.0	2.27	+1.52	+0.11
KNO_3	1.00	5.3	2.43	+1.78	0.0
KI	1.00	6.2	2.51	+1.69	+0.58
KCNS	1.00	7.2	2.33	+1.61	+1.16

Swelling $K>Na>NH_4$, $Ba>Ca>Mg$, $NO_3>I>CNS>Br=Cl$

Coagulation $K>Na>NH_4$, $CNS>I>Br>NO_3>Cl$

Discussion

Effects of temperature, particle size and redispersing the sediment once settled on the sedimentation volume of alginic acid in 3 N potassium chloride solution shown in Table 1 and 2 seem to indicate the effects of coagulation which has a profound influence upon this phenomenon. According to Buzágh[6], the adhesion force which brings about the coagulation of particles decreases at first and then increases with the rise of temperature in aqueous solution. The coagulation degree may also increase in the case of small particles. The decrease of sedimentation volume caused by redispersing the sediment may be explained by the destruction of the structure once formed by coagulation. Decrease of sedimentation volume in water which is observed on a sample kept dry for several months, may be due to the decrease of swelling. It can be seen in Figs. 2 and 3 a that the contribution of swelling to the sedimentation volume is as a whole larger than that of coagulation in most electrolyte solutions. But in solutions of ferric chloride and thorium nitrate, coagulation is pronounced and swelling effect is weak. In fact, coagulation of particles was observed by the naked eye and the microscope in these solutions. Maxima of coagulation degree were observed at relatively small concentration of ferric chloride and thorium nitrate as shown in Fig. 3 a. These maxima corresponded to the isoelectric points which were detected by the electrokinetic potential measurement. Thus a coagulation degree can be estimated from electrokinetic data. This is similar to the cases of quartz[7] and calcium carbonate[8] powder reported by Buzágh. Increase of the electrokinetic potential is due to the adsorption of polyvalent cations on alginic acid which is evident from the comparison of potential with cation exchange amount m.

(6) A. v. Buzágh, loc. cit. (2).

Summary

The sedimentation volume and swelling degree of alginic acid in electrolyte solutions were measured and the coagulation degree was calculated from these values. It was observed that the coagulation degree showed large values, giving maxima at relatively low concentrations of ferric chloride and thorium nitrate. These maxima corresponded to the isoelectric points shown on the electrokinetic potential curve. A close correlation was seen among coagulation degree, electrokinetic potential and cation exchange amount.

The cost of this research has been defrayed from the Scientific Research Expenditure of the Ministry of Education given to one of the authors.

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(7) A. v. Buzágh, *Kolloid-Z.*, **51**, 230 (1930); **52**, 46 (1930); **76**, 2 (1936).
(8) A. v. Buzágh, *Kolloid-Z.*, **83**, 279 (1938).

Electrolytic Reduction of Aromatic Carboxylic Acids III. Reduction of Phenylacetic Acid[1]

By Shin-ichi Ono and Tadao Hayashi

(Received October 24, 1952)

In the previous papers we reported that the electrolytic reduction of benzoic acid[2] at a Pb cathode gave a benzyl alcohol. On the other hand, the reduction of cinnamic acid[3] at a Pb or a Hg cathode gave no γ-phenylpropyl alcohol but gave rise to bimolecular compounds as well as β-phenylpropionic acid.

Already Inoue[4] reported that the reduction of phenylacetic acid with a Pb cathode in the alcoholic acid solution gave a β-phenylethyl alcohol (53.4%) and a small amount of phenylpinacone. Marie[5] also reported that the carboxyl group in phenylacetic acid could be reduced to alcohol (33%), but gave no pinacone. The result of the former is different from the latter.

In this paper, it is intended to discuss the reduction of phenylacetic acid in relation to the results obtained from both benzoic- and cinnamic-acids, especially in regard to the formation of the alcohol from carboxylic acid. Another object of this study is to investigate the effect of platinized platinum cathode (Pt-Pt) in the course of the electrolytic reduction.

Experimental

(1) Materials.—Phenylacetic acid was a commercial product, and further purified by recrystallization. It had a m. p. of 76°C. Cathodes used were the same materials as in the case of previous paper.[3]

(2) Reduction Method.—The reduction, including the case of high pressure of hydrogen, was carried out in the same manner as described in the previous paper.[3] In the case of Pb, Hg and Hg-Zn cathodes, usually three times the theoretical amount of current was used.

(3) Isolation and Estimation of Products.—(i) Reduction at Pb-, Hg- and Hg-Zn cathodes When the reduction was completed, the catholyte was diluted with water, and then extracted with ether. After the evaporation of the ether, the remaining liquid was steam-distilled.

The distillate from steam-distillation was extracted again with ether. The ether solution was dried with anhydrous sodium sulfate. After the vaporization of the ether, an oily liquid was obtained. The liquid contained ethyl phenylacetate, phenylethyl alcohol and small amounts of phenylethyl phenylacetate, and the latter was distilled under diminished pressure, b. p. 110~116°/7 mm.Hg., m. p. 29°C. The oily liquid was saponified with 20% alcoholic potassium hydroxide solution, and extracted with ether. The ether solution was dried with anhydrous sodium sulfate. After the vaporization of the ether, the colorless fragrant oil was fractionated at 98~102°/11 mm.Hg. The fraction has d_4^{20} 1.0325 and n_D^{20} 1.5217 (Found: C, 78.15; H, 8.10. Calculated for $C_6H_5CH_2CH_2OH$: C, 78.68; H, 8.19%). Thus it can be regarded as phenylethyl alcohol.

The residual solution from steam-distillation was neutrallized with potassium hydroxide, and then extracted with ether. The evaporation of the ether gave a small amount oily liquid from which no pinacone compound was obtained.

(ii) Reduction at a Pt-Pt Cathode. After completing the reduction, the catholyte was diluted with water, and extracted with ether, and then dried over anhydrous sodium sulfate. After the vaporization of the ether, the remaining liquid was distilled under diminished pressure. The two fractions, (f_1) 65~80°/6 mm.Hg and (f_2) 114~119°/6 mm.Hg were obtained.

Redistillation of (f_1) gave a liquid, b. p. 68~70°/6 mmHg. d_4^{25} 0.9475, n_D^{25} 1.4472. The fraction (f_1) was saponified with 20% alcoholic potassium hydroxide solution, and extracted with ether. The ether solution was dried with anhydrous sodium sulfate. After the vaporization of the ether, the residual liquid was distilled under diminished pressure. The fraction has 117~119°/6 mm.Hg, d_4^{25} 0.9953, n_D^{25} 1.4590 (Found: C, 67.52; H, 9.79. Calculated for $C_6H_{11}CH_2COOH$: C, 67.60; H, 9.86%). Thus the fraction (f_1) can be regarded as ethyl cyclohexylacetate.

The fraction (f_2) was distilled again under diminished pressure, and gave a liquid, b. p. 117~119°/6 mmHg, d_4^{22} 0.9955, n_D^{22} 1.4588 (Found: C, 67.73; H, 9.78. Calculated for $C_6H_{11}CH_2COOH$: C, 67.60; H, 9.86%). Thus it can be regarded as cyclohexylacetic acid.

(1) This paper was presented at the regular meeting of the Chemical Society of Japan, held at kyoto, on May, 1951.
(2) S. Ono and T. Yamauchi; *This Bulletin*, **25**, 404 (1952).
(3) S. Ono and T. Hayashi; ibid. **26**, 11 (1953).
(4) H. Inoue; *J. Soc. Chem. Ind. Japan*, **24**, 914 (1921).
(5) M. Marie; *Bull. Soc. Chim.*, **25**, 512 (1919).

Results and Discussions

(1) Formation of Phenylethyl alcohol.—The optimum conditions for the preparation of phenylethyl alcohol from phenylacetic acid at a Pb cathode are shown in the Table 1.

Table 1

Optimum conditions for the formation of phenylethyl alcohol

Investigator	$PhCH_2$-COOH (g.)	EtOH (cc.)	H_2SO_4 (%) (g.)	Current quantity (A. hrs.)	Yield (%)
Marie[5]	20	20	50 50	40	33
Inoue[4]	20	20	75 70	40	53.4
Authors	13.6	40	50 50	30	28
〃	13.6	40*	50 50	30	35.3

Current density: 10 amp/dm.^{2} Temp: 60°C.

*, Cellosolve was used as a solvent instead of EtOH.

It is a well-known fact that the ester compound is not suitable for the preparation of the corresponding alcohol by the electrolytic reduction, as is seen in the case of benzoic acid.[6] Comparing the results of Table 1, it is surprizing that Inoue's condition gave the yield higher of alcohol, even though his condition seems to be more likely to give the ethyl phenylacetate than those of other's.

In the present experiment, it was found that the cellosolve is available as a solvent to avoid the formation of ester compound.

We have found that the electrolytic reduction of the carboxyl group is most easily possible when it is directly attached to an aromatic ring in a series of carboxylic acid, such as benzoic acid. In the case of phenylacetic acid, the carboxyl group is isolated by the CH_2-linkage from the phenyl group; therefore, it is expected that the electronic interaction between phenyl and carboxyl groups would be less effective than in the case of benzoic acid. That is, the yield of alcohol from phenylacetic acid is smaller than that from benzoic acid. Cinnamic acid or phenylpropionic acid gave no γ-phenylpropyl alcohol as stated in the previous paper.[3] It may be expected that the relative ease of the reduction of carboxyl group is closely related to the nature of R-groups. (R=Ph-, $PhCH_2$- or $PhCH_2CH_2$-)

(2) Effect of Cathode.—In the present experiment, lead (Pb), zinc amalgam (Hg-Zn), mercury (Hg) and platinized-platinum (Pt-Pt) cathodes were used in order to determine the effect of cathode materials on the reduction products. Pb, Hg-Zn and Hg cathodes were observed to act analogously, giving the phenylethyl alcohol.

We have found that Pb cathode is preferable to Hg-Zn or Hg cathode, for the formation of phenylethyl alcohol.

On the other hand, the reduction at a Pt-Pt cathode gave rise to cyclohexyl compounds and it seemed that the behavior of the Pt-Pt cathode was quite the same as in the case of benzoic-and cinnamic-acids.[7]

(3) Effect of Solvents.—(i) **Reduction at a Pb Cathode** When sulfuric acid and ethanol are used as a catholyte, we have found that the 50% of sulfuric acid solution is available for the formation of phenylethyl alcohol. In the case of high concentration of sulfuric acid solution, the yield of phenylethyl alcohol is decreased by the formation of ethyl phenylacetate which will be less reactive for the formation of phenylethyl alcohol. We have studied that when 75% of sulfuric acid and ethanol are used as a catholyte, more than 60% of phenylacetic acid is esterified without using the current at 60°C.

To avoid the esterification, ethyl acetate and cellosolve were used as a solvent, and the later gave the better yield. Results are shown in the Table 2.

Table 2

Effect of Solvents

Catholyte: Phenylacetic acid 13.6 g, Sulfuric acid 40 cc., Solvent 40 cc. Current density: 10 amp/dm.^{2} Current quantity: 30 A·hrs. Cathode: Lead (1.0 dm.^{2})

Run No.	Solvent	Temp. (°C.)	Phenylethyl alcohol (%)
1	MeOH	50	25.0
2	EtOH	60	28.0
3	$CH_3COOC_2H_5$	60	29.0
4	$C_2H_5OCH_2CH_2OH$	60	35.3

Table 3

Effect of Acid concentration

Catholyte: Phenylacetic acid 13.6 g, EtOH 40 cc., Sulfuric acid 40 cc. Cathode: Pt-Pt sheet (1 dm.^{2}). Current quantity: 28 A. hrs. (Theor. 16.1 A. hrs.). Temperature: 30~35°C.

Conc. of H_2SO_4%	C. D. amp/dm.^{2}	product f_1 (g.)	f_1 (%)	f_2 (g.)	f_2 (%)	Yield f_2(Total)* (%)	C. E. (%)
28	2	6.0	35.3	6.0	42.3	79.4	45.7
50	2	9.5	55.9	3.0	21.1	77.9	44.8
75	2	10.5	61.8	1.5	10.6	72.8	41.9

Products: f_1; Ethyl cyclohexylacetate.
f_2; Cyclohexylacetic acid.

* Sum of f_2 and cyclohexylacetic acid produced from the hydrolysis of f_1.

(6) (a) For example, Swann, *Trans. Electrochem. Soc.* **75**, 411 (1939), and reference (2).
(b) S. Ono and J. Nakaya reported at the regular meeting of the Chemical Society of Japan held at Tokyo, April, 1951. that the electrolytic reduction of ethyl phenylacetate at Pb cathode gave no phenylethyl alcohol.

(7) c. f. Part I and II of this series, ref. (2) and (3).

(ii) **Reduction at a Pt-Pt Cathode** It was seen from the data in the table 3 that the yield of ethyl cyclohexylacetate was increased and the yield of cyclohexylacetic acid was decreased with the increase of the acid concentration. In the same acid concentration, it was found that better yields could be obtained at a lower current density (Table 4).

Table 4
Effect of Current Density

Catholyte: Phenylacetic acid 13.6 g, EtOH 40 cc., 50 % sulfuric acid 40 cc. Cathode: Pt-Pt sheet (1 dm.^{2}). Current quantity: 28 A. hrs. (Theor. 16.1 A. hrs.). Temperature: 30~35°C.

C. D. (amp/dm.^{2})	Yield (%)	C. E. (%)
0.5	81.5	46.9
1.0	80.2	44.1
2.0	76.5	44.0
3.0	74.6	42.9
4.0	75.5	43.4
5.0	75.5	43.4

Product; Cyclohexylacetic acid.

(4) **Effect of High Pressure.**—In a series of this investigation, the special study was made in order to know the effect of external pressure in the course of electrolytic reduction of phenylacetic acid.

Table 5
Effect of high pressure

(a) Reduction of Phenylacetic acid at a Pb Cathode

Catholyte: Phenylacetic acid 13.6 g., Sulfuric acid 40 cc., Cellosolve 40 cc. Cathode: Lead sheet (1 dm.^{2}). Current quantity: 30 A. hrs. (Theor. 10.7 A. hrs.). Temperature: 50~55°C.

H_2SO_4 (%)	C. D. (amp/dm.^{2})	Press. of H_2 (atm.)	Yield (%)	C. E. (%)
50	5.0	—	34.0	11.7
〃	〃	25	32.5	11.6
〃	〃	35	33.8	12.0
75	5.0	—	25.5	9.1
〃	〃	40	26.4	9.4
〃	10.0	40	32.4	11.5
28	5.0	—	30.3	10.8
〃	〃	20	31.5	11.2
〃	10.0	40	32.8	11.7

Product: Phenylethyl alcohol.

The reduction was undertaken at the high pressure of hydrogen (15~40 atm.). In the case of the reduction at a lead cathode, the product was quite the same as the ordinary pressure. Results are given in the Table 5. Among these data, a slight increase in the product was observed at the high pressure, but an increase of the hydrogen pressure made no clear effect on the product. If, in the case of Pt-Pt cathode, we may assume that the reduction consists mainly in the catalytic mechanism, it can be expected that there is some correlation between the reduction products and the external pressure. But we have fairly comparable data in this experiment; (Table 6), therefore, further studies must be made to clarify this problem.

Table 6
Effect of high pressure

(b) Reduction of phenylacetic acid at Pt-Pt Cathode.

The electrolytic conditions are the same as table 4, except the external pressure of hydrogen.

C. D. (amp/dm^2)	Press. of H_2 (atm.)	Yield (%)	C. E. (%)
3·0	—	74.6	42.9
〃	15	75.5	43.4
〃	30	76.0	43.7
4.0	25	76.8	44.2
〃	35	76.0	43.7
5.0	25	78.2	45.0
〃	40	79.0	45.4

Product: Cyclohexylacetic acid.

Summary

(1) The electrolytic reduction of phenylacetic acid at a Pb, a Hg-Zn, a Hg or a Pt-Pt cathode was studied. It was confirmed that phenylethyl alcohol could be produced from phenylacetic acid using Pb, Hg-Zn and Hg cathodes. The Pt-Pt cathode was observed to behave catalitically in the course of reduction and gave rise to cyclohexylacetic acid.

(2) The relative ease of the reduction of the carboxylic acid to alcohol was closely related to the nature of the group which lies between phenyl and carboxyl radical.

(3) The effect of high pressure of hydrogen was discussed on the electrolytic reduction of phenylacetic acid.

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Dichroic Study on Polyvinylalcohol Fiber
III. Double Refraction of Polyvinylalcohol Fiber

By Saburo OKAJIMA, Yasuji KOBAYASHI and Ryuzo YAMADA

(Received November 6, 1952)

In the preceding paper the change of the dichroism of the model filament of polyvinylalcohol (PVA) by stretching is reported. Now the intrinsic double refraction of the same filament after stretching and heat-treatment under various conditions is given. As the dichroism and intrinsic double refraction can indicate the orientation of the molecules and it is known that the double refraction of the fiber is affected by the crystallinity, so there may be a possibility to know separately these two factors, the orientation and the crystallinity, by comparing these two measures.

In this report the double refraction of PVA filament which has previously been treated variously was observed as the preliminary experiment on the determination of the above two factors.

Experiment

(I) Preparation of the isotropic model filament and the method of stretching.—The isotropic filament of PVA was melt-spun as described in the first report of this study.[1] The stretching of the isotropic model filament was also carried out similarly as previously,[2] but now it is known that a filament is not stretched uniformly along the axis and this is not due to the irregular structure of the sample but to the stretching conditions. This is clearly shown by the following experiment: A pair of filaments, *a* and *b*, in Fig. 1, on which many small points had been marked with a special ink, were attached parallel to a stretching frame and stretched under various conditions and the degrees of stretching were observed along their axes by comparing the corresponding distances between the marks before and after stretching. Fig. 1 shows the distribution of the stretching degree (v) along the axes of a pair of filaments which had been attached to the same frame and, therefore, stretched at the same time. We can see from the figure some interesting facts, as follows:

(a) The end parts near the clamps are elongated more and the middle part is comparatively uniform. The tendency becomes remarkable as the total stretching degree grows larger.

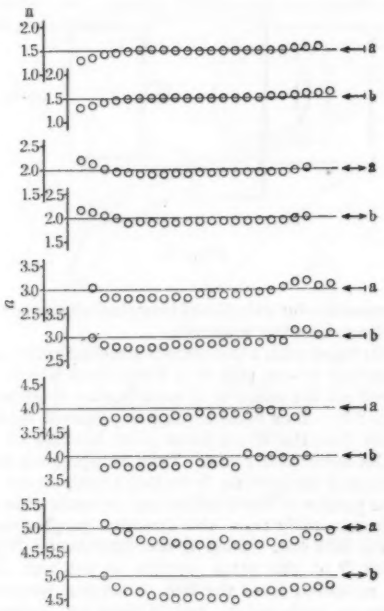

Fig. 1.

(b) The correspondence of the stretching of the two parallel filaments, *a* and *b*, is very good irrespective of the irregularity of deformation above. So the phenomenon is not caused by the irregular structure of the sample along the axis.

(c) The distribution of v along the filaments is nearly symmetrical. This is irrespective of the fact that either both ends of the filament are pulled away or only one end is pulled away, fixing the other end. These types of stretching are shown by ←→ and → in the figure.

Taking this irregularity into consideration, the test pieces used for the measurements of the intrinsic double refraction (Γ) and v were taken from the middle part of the stretched filament in the following experiments.

(II) Determination of Γ.—Some test pieces taken from the middle part of the stretched filament was comented to a frame prepared from a brass plate of 0.4 mm thickness (Fig. 2 a). A

(1) S. Okajima and Y. Kobayashi, *J. Soc. Chem. Ind. Japan*, **54**, 791 (1951).
(2) S. Okajima and Y. Kobayashi, This Bulletin, **25**, 268, (1952).

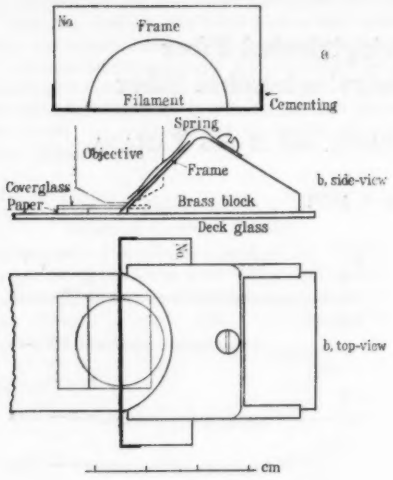

Fig. 2.

benzene-alcohol solution of benzylcellulose was used as the cementing material.

This frame with a test piece is attached with a pair of springs to one side of a brass block which was placed on the stage of a polarization microscope (Fig. 2 b). This brass block was prepared in such a way that the above brass plate inclines by 45° to the horizontal plane. Then dropping the brass plate and reattaching it to the block, nearly the same portion of the filament can be again observed microscopically from the direction perpendicular to the first one. Then if the retardation R and width D of the same portion of the test piece are measured from the two directions perpendicular to each other, and if these two measures are R_1, D_1 and R_2, D_2, then Γ of that part is given by R_1/D_2 and R_2/D_1. The suffixed 1 and 2 mean the first and second measurements.

If the filament is not exactly circular, then D_1 differs slightly from D_2 and the above device gives a good result. Furthermore, when the section of the filament is too elliptic and the cover glass is pressed slightly, the filament against the deck glass owing to the surface tension of the mountant, the larger diameter is liable to be observed under a microscope, so now it is devised to insert a piece of paper of an appropriate thickness between the cover and deck glasses to give a sufficient space for the filament to take a free state.

The mountant was prepared by adding some cedar oil to tricresylphosphate to adjust the refractive index to that of PVA, 1.535. This mountant is vaporisable with difficulty and very suitable for our purpose.

The sample was stocked in a vacuum P_2O_5-desiccator over 15 hours and mounted in the above liquid. The magnification of the microscope was 400×.

The measurment of the retardation was carried out as usual partly by observing the diffraction colour and partly by using compensater, using D-line, as the light source.

Experimental Results

The samples were conditioned at the various humidities at 20° and 30°C. and stretched under the same conditions. They were treated as described above and the change of the double refraction by stretching were observed. The result is shown by the curve (a) in each figure below. Some of the samples were washed out with carbon tetrachloride or ether to remove the mountant and then heated in an air-oven controlled at 140 ±3°C. for various periods of time, after being conditioned in a desiccator containing the saturated solution of ammonium sulfate (81% RH at 20°C.). Some of them were washed, conditioned and heated again and again and the change of their Γ by the heat treatment were traced. The results are summarised below.

Fig. 3 shows the carried out result of experiment at 30°C. and 100% RH. The curve a is the relation of Γ versus v, which is a saturation type. The points ○ and ● are obtainde by two different observers with using two samples spun separately, but they coincide well; therefore, the reproducibility of the experiment can be said to be very good.

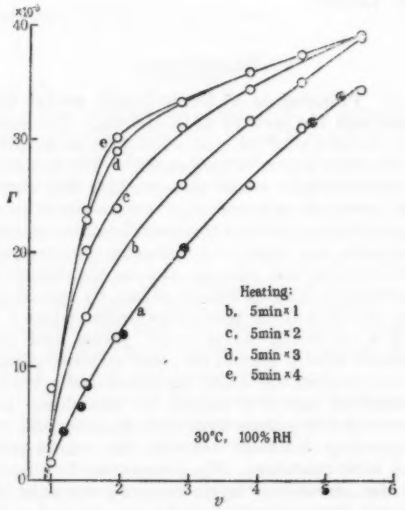

Fig. 3.

The curve b (5 min. heating ×1) is almost parallel to a and the others c~e are not parallel but their end points converge to one point and only the middle parts rise stepwise in the order c to e. Therefore the increment of Γ by heating at 140°C. is not uniform relative to v, but the change is largest at $v \fallingdotseq 2$ and the filament of the highest orientation attains the equilibrium state

after short heating, while some four heatings are required at $v \fallingdotseq 2$.

Fig. 4~7 show the similar experiments stretched at 30°C. and 93% RH, at 20°C. and 100% RH, at 20°C. and 93% RH, at 20°C. and 81% RH respectively. The character of each case is similar to that of Fig. 3. The saturated state is obtained by heating for 15~30 min. in all experiments.

In the case of Fig. 6 the sample b' was heated for 15 min. immediately after vacuum drying and had not been conditioned, and the curve b' is somewhat lower than the corresponding curve b, which was heated after the ordinary conditioning. The curves b and b' shift to c and c' respectively by the secondary heating of 15 min. after ordinary conditioning, where c' is also below the corresponding c. Therefore some amount of moisture in the filament seems to have a good effect upon the raising of Γ, although the moisture in the filament vaporises rapidly in such an open heating. The phenomenon is not the problem of the rate of change and it remains after reaching the equilibrium state.

The stretching at 20°C. and 81% RH is very poor as shown in Fig. 7; this fact has been pointed out already in the previous paper with using dichroism.

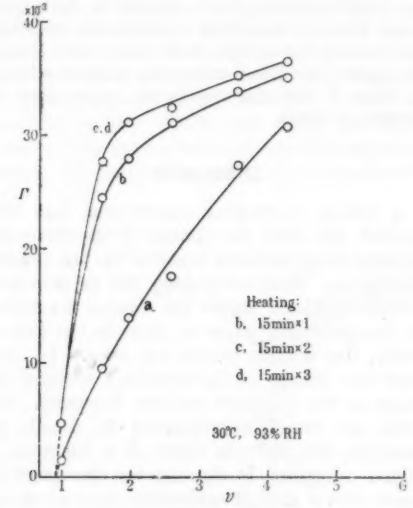

Fig. 4.

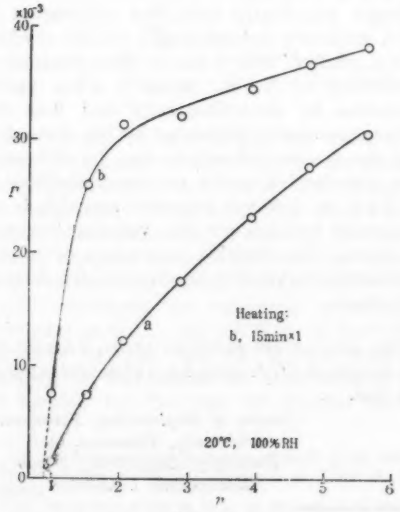

Fig. 5.

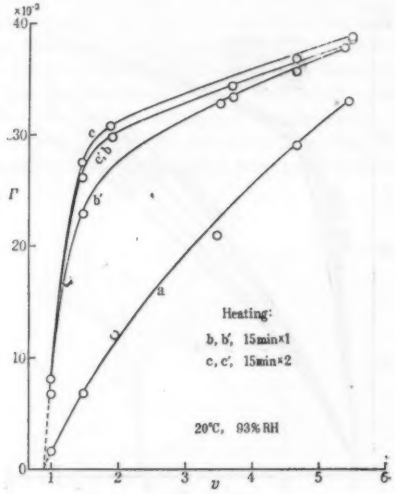

Fig. 6.

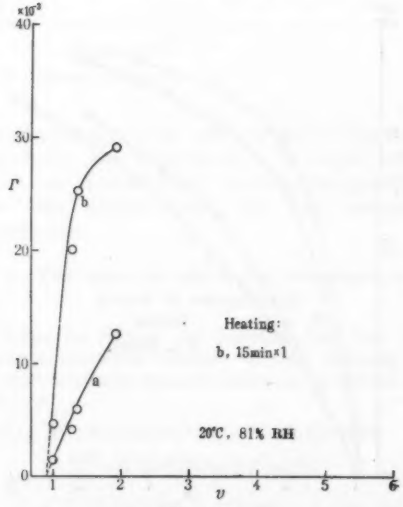

Fig. 7.

Now summing up the curve a and the one heated to equilibrium in each experiment, it is indicated as shown in Fig. 8, that the rise of Γ by stretching becomes sharper as the stretching is carried out at lower humidity and higher temperature, while the difference disappears when these samples are heated to equilibrium and the original curves converge nearly to one relation, where the maximum value of Γ amounts to $38\sim39\times10^{-3}$.

Now an experiment was made, in which the filament stretched at 20°C. and 100% RH were heated at 140°C. for 25 min., when one half of it (b) was treated as before but immediately after vacuum drying, while the other half (c) was heated at the same temperature after conditioning at 20°C. and 81% RH and at the higher humidity by supplying the water vapor. As shown in Fig. 9 the moisture effect is clearly recognized here also, but the effect is not similar to the case of Fig. 6 and it is in the reverse direction and, therefore, the optimum moisture content seems to exist for the raising of Γ. The difference here is also considered, not to be caused by the different rate of change as the effect remains in the equilibrium state, which is attained by repeating the heat-treatment for 60 min.

In this experiment also a filament (●) was stretched very slowly (8 hours were required for the total stretching) as compared to the experiment hitherto described, in which the stretching was carried out within 10 seconds. According to the figure the slower stretching is more effective to raise Γ but the maximum value does not change so much.

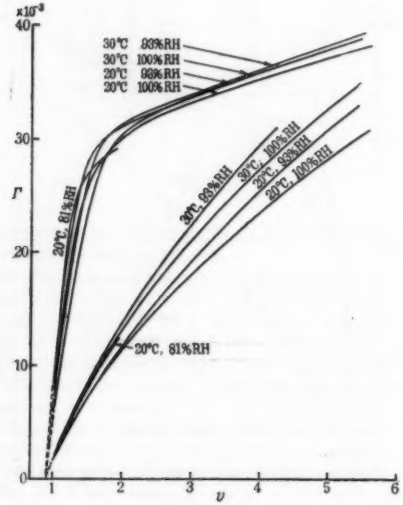

Fig. 8.

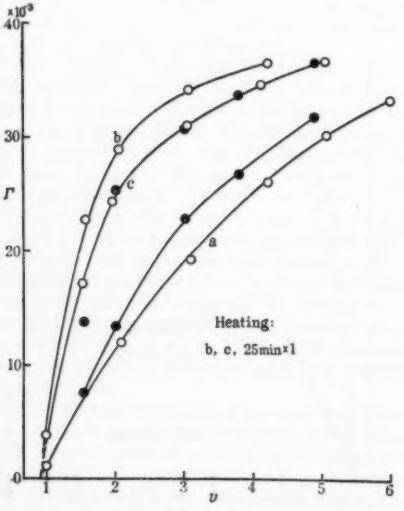

Fig. 9.

Discussion

A similar stretching experiment has been carried out and the change of the dichroism by stretching has been reported in the preceding paper. Now comparing the experimental results obtained under the similar conditions in the preceding paper to these in the present study, the similar trends are seen. In both cases the change of the measures becomes less sharp as the moisture content increases. But there are small discrepancies in detail; for example, the dichroic curve of a filament of higher moisture is sigmoid but the birefringence curves are all saturation type as shown above.

This is certainly because the dichroic data indicate principally only the orientation of PVA molecules independently on the crystallinity, while Γ relates also to the crystallinity. According to K. H. Meyer[3] PVA partly crystallize by stretching only and then the orientation curves indicated by the dichroism and the double refraction may be different. But quantitative study on the crystallization of PVA is not yet reported and this is an important problem for the vinylon industry of Japan. The detailed comparison of the two orientation curves will be given in the following paper.

The authors are indebted to Dr. Yazawa for the sample of PVA used, for which their thanks are due.

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(3) K.H. Meyer, "Natural and synthetic high polymers."

The Resonance Energy and the Hindering Potential Barrier of the C-C axis of Glyoxal

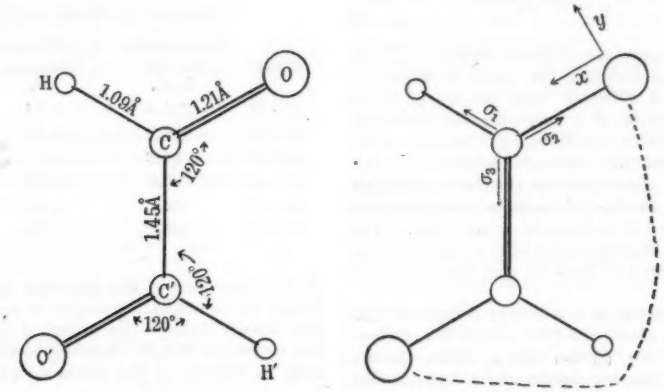
By Mikio KATAYAMA

(Received November 6, 1952)

Introduction

There have been few investigations on the hindering potential about single bonds of aliphatic compounds which have conjugated double bonds. In these compounds the molecular structures are so remarkably influenced by quantum-mechanical resonance, that the potential barrier about the bond has to be calculated by taking into account the resonance energy. The hindering potential of butadiene[1] was discussed by calculating the energies of several structures of butadiene, by the method of Goeppert-Mayer and Sklar, but owing to the uncertainty of the correction of the energy zero of these structures, it was not possible to obtain a precise value of the hindering potential. On the other hand, Penny and Sutherland[2] calculated the hindering potential of O-O axis in H_2O_2 and of N-N in H_2N-NH_2 molecule by the use of Heitler-London's method. In this article the same method will be applied for the case of glyoxal having conjugated double bonds.

By electron diffraction investigation the stable structure of glyoxal molecule was determined to be planar and of the trans[3] form. Accordingly, in order to calculate the hindering potential barrier of glyoxal, it is sufficient to compute the difference between the energies of the perpendicular form and of the planar one. For the stable planar configuration the structure *A* and the structure *B* in Fig. 1 are considered as the possible non-polar resonance structures, while for the perpendicular configuration, the structure *B* is to be put aside from our consideration, since in this position the two double bonds do not resonate absolutely.



Structure A Structure B

Fig. 1.—The Configuration of Glyoxal molecule

§ 1. The case in which the structure a alone is considered

When we assume the molecule has only the form A, the wave function of this molecule in Heitler-London's approximation is expressed as follows:

$$\Psi_A = \{\phi^O{}_y(1)\phi^O{}_y(2)\}(\phi^H(3)\psi_{\sigma_1}(4))(\phi^O{}_\pi(5)\psi_{\sigma_2}(6))$$
$$(\phi^O{}_\pi(7)\phi^C{}_\pi(8))(\phi_{\sigma_3}(9)\phi'_{\sigma_3}(10))$$

(1) M. Katayama and Y. Morino; *Reports of the Institute of Science Technology, University of Tokyo*, **5**, 19, (1951).

(2) W. G. Penny and G. B. B. M. Sutherland: *J. Chem. Phys.*, **2**, 492 (1934).

(3) J. E. Lu Valle and V. Schomaker: *J. Am. Chem. Soc.*, **61**, 3520 (1939).

$$\{\phi^{O}_{y'}(11)\phi^{O}_{y'}(12)\}(\phi^{H'}(13)\phi_{\sigma_1'}(14))$$
$$(\phi^{O}_{x'}(15)\phi_{\sigma_2'}(16))(\phi^{C}_{\pi'}(17)\phi^{C}_{\pi'}(18)) \quad (1)$$

where bracket { } means a lone pair, and bracket ( ) a pair bond: for example,

$$(\phi^{H}(3)\phi_{\sigma_1}(4)) = \frac{1}{2}(\phi^{H}(3)\phi_{\sigma_1}(4)$$
$$+\phi^{H}(4)\phi_{\sigma_1}(3))(\alpha(3)\beta(4)-\alpha(4)\beta(3)) \quad (2)$$

and ϕ^{H} denotes the wave function of hydrogen, and ϕ_{σ_1}, ϕ_{σ_2} and ϕ_{σ_3} the hybridized wave functions of carbon atoms. The wave functions of π-electrons of oxygen and carbon atoms are designated by ϕ^{O} and ϕ^{C}_{π}, the directions of the coordinate axis being shown in Fig. 1. In this expression, 1s electrons of carbon atoms and 1s and 2s electrons of oxygen atoms are ignored. Thus in this approximation the energy of certain states of the molecule may be expressed by the following formula:

$$W = H(E) - 2\sum J_{pp'} - \sum J_{pt} + \sum J_{qr} - \frac{1}{2}\sum J_{rs} - \sum_{u} J_{tt'} \quad (3)$$

where $H(E)$ denotes the coulomb energy, $J_{pp'}$ the exchange energy between the wave functions of the electrons of different lone pairs, J_{pt} those between an electron of a lone pair and the other electron which does not belong to the lone pair, J_{qr} those between the electrons which make the same bond, J_{rs} those between the electrons which make different bonds, $J_{tt'}$ those between electrons which do not make a bond or a lone pair. u is the element of representation of symmetry group. The last term will be used in the calculation on §2.

In order to calculate the energy difference due to the rotation about the C-C axis, it is sufficient to ignore from Eq. (2) the terms which do not vary with the rotating angle about the central C-C axis. Thus the remaining energy may be expressed as follows:

$$\begin{aligned} W(\varphi) = 4\{&U(yO : yO') + U(yO : H') + U(yO : xO') \\ &+ U(yO : \sigma_2') + U(yO : O\pi') \\ &+ U(yO : C\pi') + U(yO : \sigma_1')\} \\ +2\{&U(H : \sigma_1') + U(H : xO') + U(H : \sigma_2') \\ &+ U(H : O\pi') + U(H : C\pi') + U(\sigma_1 : xO') \\ &+ U(\sigma_1 : \sigma_2') + U(\sigma_1 : O\pi') + U(\sigma_1 : C\pi') \\ &+ U(xO : \sigma_2') + U(xO : O\pi') + U(xO : C\pi') \\ &+ U(\sigma_2 : O\pi') + U(O\pi : C\pi') + U(\sigma_2 : C\pi')\} \\ &+ U(H : H') + U(\sigma_1 : \sigma_1') + U(xO : xO') \\ &+ U(\sigma_2 : \sigma_2') + U(C\pi : C\pi') + U(O\pi : O\pi') \end{aligned} \quad (4)$$

where $U(a:b) = Q(a:b) - \frac{1}{2}J(a:b)$. The coulomb and the exchange energies, $Q(a:b)$ and $J(a:b)$, have respectively the following expression:

$$\left.\begin{aligned} Q(a:b) &= \int \phi_a(1)\phi_b(2)\, H\phi_a(1)\phi_b(2)d\tau \\ J(a:b) &= \int \phi_a(1)\phi_b(2)\, H\phi_a(2)\phi_b(1)d\tau \end{aligned}\right\} \quad (5)$$

where H means Hamiltonian of $(a:b)$ system. It would be desirable to calculate the integrals, but unfortunately, the tables of these integrals given by Kotani[4] et al, are not available for this case, because the integrals to be used in the present calculation are those between the atoms farther apart than those given in their tables. Hence, for simplicity, the coulomb energy is assumed to be 20% of the Morse function and the exchange energy the remaining part of the Morse function. The dissociation energies,[5] the equiliblium distances and the vibrational frequencies are listed in Table 1, which are used to calculate the Morse functions. For the exchange integral between the π-electrons the value calculated by Penny[6] in ethylene molecule, 0.75 e. v., is used.

Table 1
Constants for Morse function

Bond	Dissociation Energy kcal.	Equilibrium Distance A.	Frequencies $cm.^{-1}$
H—H	102.4	0.74	4375
O—H	113.1	0.97	3660
O—O	34.3	1.32	1304
C—O	81.8	1.43	1030
C—C	83.0	1.54	990
C—H	92.3	1.10	2930

If the directions of the bondings of the two different atoms make the angles θ_1 and θ_2 with the line drawn through the nuclei of the two atoms, the exchange integral between these two electrons may be written in the following expression:

$$J(xO : xO') = J'(xO : xO')\cos^2\theta_1\cos^2\theta_2 + J_{\perp}(xO : xO')\cos\varphi\sin^2\theta_1\sin^2\theta_2 \quad (6)$$

where $J'(xO : xO')$ represents the exchange integral derived from Morse function, and $J_{\perp}(xO : xO')$ means the one between the perpendicular components of the wave functions to the O—O line. In order to estimate the value of $J_{\perp}(a:b)$, if both electrons, a and b, are referred to p-electrons, $J_{\perp}(a:b)$ has the same value as the exchange energy between π-electrons, and if a and b are referred to p-electron and hybridized sp^2-electron respectively, or both of them are referred to hybridized sp^2-electrons, the values of $J(a:b)$ are taken as 2/3 or 4/9 as those of π-electrons. φ represents the angle of rotation

(4) M. Kotani et al: *Proc. Phys-Math. Soc.*, **20**, Extra No. (1938); **22**, Extra No. (1940).
(5) R. H. Gillette and A. Sherman: *J. Am. Chem. Soc.*, **58**, 1135 (1936).
(6) W.G. Penny: Proc. *Phys. Soc. London*, **46**, 333 (1934).

about the C—C axis, the zero of the angle being at the position where the molecule has the planar trans form. The calculated energies of the planar and perpendicular models of glyoxal by the method stated above are listed in Table 2. It is well established by this calculation that, if this molecule has the wave function Ψ_A only, i. e. if only the type A of molecule exists, the perpendicular form is more stable than the planar one.

§ 2. The case of the resonance between the structure A and B

It is evident that the molecule of the glyoxal has not only the contribution of the structure A, but also of other forms such as the structure B. In this paragraph the calculation is performed, considering the structure A and B as the resonance form. The structure B is represented by the following wave function:

$$\begin{aligned}\Psi_B = &\{\phi^{C}_{y}(1)\phi^{O}_{y}(2)\}(\phi_{\sigma_1}(3)\phi^{H}(4))(\phi_{\sigma_2}(5)\phi^{O}_{x}(6))\\ &(\phi_{\sigma_3}(7)\phi_{\sigma_3'}(8))(\phi^{C}_{\pi}(9)\phi^{C}_{\pi'}(10))\\ &\{\phi^{C}_{y'}(11)\phi^{O}_{y'}(12)\}(\phi_{\sigma_1'}(13)\phi^{H'}(14))\\ &(\phi_{\sigma_3'}(15)\phi^{O}_{x'}(16))(\phi^{O}_{\cdot}(17)\phi^{O'}_{\pi}(18))\end{aligned} \tag{7}$$

As the result of the resonance between the structure A and B, the energy of the molecule is calculated from the following secular equation,

$$\begin{vmatrix} M_{11}-W & M_{12}-\frac{1}{2}W \\ M_{12}-\frac{1}{2}W & M_{22}-W \end{vmatrix} = 0 \tag{8}$$

$$M_{11} = Q + 2J(O\pi : C\pi) - \frac{1}{2}\{J(O\pi : O\pi') + J(C\pi : C\pi')\}$$

$$M_{12} = \frac{1}{2}M_{11} + \frac{3}{4}\{J(C\pi : C\pi') + J(O\pi : O\pi')\} - \frac{3}{2}J(C\pi' : O\pi)$$

$$M_{22} = Q + J(C\pi : C\pi') + J(O\pi : O\pi') - J(C\pi : O\pi)$$

In this equation, M_{11} is the energy of the molecule when only the structure A is considered. The result of this calculation indicates that the energy of the ground state in the trans form is about 5.12 kcal. lower than the case of the structure A alone considered, if the resonance between two non-polar structures is considered. It will be evident that the cis-form is also stabilized by the resonance which has almost the same energy, so that the same amount of resonance energy is tentatively assumed for the cis-form. The calculated value of the energy of each form is shown in the lower part of Table 2. It can easily be seen that the planar form is more stable than the perpendicular one.

Table 2

Relative Energies of Several Configurations

	trans form	cis form	perpendicular form
Structure A only considered	33.72 kcal.	32.83 kcal.	30.13 kcal.
Resonance between the structures A and B being considered	28.60	27.71	30.13

Discussion and Acknowledgement

The calculation stated above indicates that the structure A gives the more stable perpendicular form than the planar ones, while the resonance between A and B makes the planar one more stable than the perpendicular one. Thus it may be concluded that the cons deration of the conjugation of double bonds contributes several kilocalories to the hindering potential about the central single bond, while the energy of the perpendicular form is the same as that in the case where only the form A is considered. The hindering potential of glyoxal has not been determined experimentally, but in the molecules of oxalyl-chloride it was confirmed by electron diffraction and dipole moment measurements[7] that the hindering potential is about 5 kcal., the trans-form being the most stable position. The value 1.5 kcal. ~2.4 kcal. obtained in this article is practically of the same order.

This calculation indicates that the cis-form is more stable than the trans-form, contrary to the observed result. This disagreement might be due to the approximate nature of the calculation; for instance, to the exclusion of the 1s and 2s electrons of O atoms. Moreover, it would be reasonable to take into account the polar structure as one of the canonical set. But, the higher order approximation as this ought not to be performed since the values J and Q used in this calculation are comparatively rough.

The author takes this best opportunity to express his real appreciation for the valuable advice and understanding of Prof. Yonezo Morino and Assistant Professor Saburo Nagakura.

Department of Chemistry, Faculty of Science, Tokyo University

(7) Y. Morino et al: unpublished.

Dipole Moments of Bromotropolones, Thujaplicins and Related Compounds*

By Yukio KURITA, Tetsuo NOZOE and Masaji KUBO

(Received November 11, 1952)

We have already measured the dipole moments of tropolone and some of its derivatives,[1][2][3] and discussed the results in relation to the molecular structure of these compounds and to the electronic structure of tropolone as derived from molecular orbital treatment. The present investigation was undertaken in order to determine the position of substituents in seven new kinds of tropolone derivatives synthesized by one of us (Nozoe) and his collaborators. From the studies on magnetic susceptibility, Hazato and his collaborators suggested that tribromotropolone lacks aromatic properties characteristic of tropolone derivatives.[4] We hoped that the dipole moment measurement would reveal some feature of interest concerning the peculiarity of this compound. Nozoe has reported that unlike other tropolone derivatives α-thujaplicin forms two kinds of crystals of different melting points.[5] It seemed to be interesting to decide whether the difference of the two forms is due merely to the arrangement of molecules in crystals or whether the two crystals are made up of molecules of different molecular structure such that they give different dipole moments in solution.

Experimental Method and Results.—All the measurements were made in benzene solution at 25°C. The dielectric constant was measured with the apparatus reported in the previous paper.[1] The materials used were synthesized and purified in the laboratory of organic chemistry in Tohoku University. The amount of each sample at our disposal was less than 0.3 g. and we were obliged to be satisfied with measurements on solutions of a few different concentrations. As some of these compounds were hygroscopic, we employed a modified Hedestrand method similar to that introduced by Halverstad and Kumler[6] for obtaining specific polarization $p_{2\infty}$ at infinite dilution, differing in the fact that densities were used rather than specific volumes.

$$p_{2\infty}=p_1+C\alpha-\frac{p_1}{d_1}\beta \qquad (1)$$

Here p_1 and d_1 denote the specific polarization and density of the solvent, α and β are the rates of change of the dielectric constant ε and density d with weight fraction w,

$$\varepsilon_{12}=\varepsilon_1+\alpha w_2,\quad d_{12}=d_1+\beta w_2 \qquad (2)$$

and

$$C=3/d_1(\varepsilon_1+2)^2 \qquad (3)$$

where the suffixes 12, 1 and 2 signify the solution, solvent and solute respectively. The crucial data affecting the value of $p_{2\infty}$ were α and β. In evaluating the values for these two constants with equation (2), we used the data on solution alone to minimize the possible effect of moisture content. The probable errors $\delta\alpha$ and $\delta\beta$ estimated by least square method gave for the probable error $\delta p_{2\infty}$ the value

$$\delta p_{2\infty}=C\,|\,\delta\alpha\,|+\frac{p_1}{d_1}\,|\,\delta\beta\,| \qquad (4)$$

The probable error $\delta\mu$ in dipole moments was due partly to the assumption that the sum of the electronic and atomic polarization P_E+P_A is equal to the molecular refraction calculated for D-line. Shiratori and Kinumaki[7] reported that the exaltation of molecular refraction is fairly great in these compounds. The atomic polarization of these compounds is supposed to be high owing to the possible vibration of a proton participating in hydrogen bond formation. Fortunately orientation polarization is in general much higher than P_E+P_A in the present case, hence the errors in P_E and in P_A do not affect the value for the moments in an appreciable manner. The results of measurements together with the estimated* errors are given in Tables 1 and 2.

* Read before the scientific meeting of the Chemical Society of Japan held on July 5, 1952.

(1) Y. Kurita, T. Nozoe and M. Kubo, This Bulletin, **24**, 10 (1951).

(2) Y. Kurita and M. Kubo, ibid., **24**, 13 (1951).

(3) Y. Kurita, T. Nozoe and M Kubo, ibid., **24**, 99 (1951).

(4) G. Hazato, J. Maruha, T. Ikegami and H. Kon, reported at the annual meeting of the Chemical Society of Japan on April 8, 1951.

(5) T. Nozoe, Y. Kitahara, K. Yamane and T. Ikemi, *Proc. Japan Acad.*, **27**, 193 (1951).

(6) I. F. Halverstadt and W. D. Kumler, *J. Am. Chem. Soc.*, **64**, 2988 (1942).

(7) K. Shiratori and S. Kinumaki, reported at the annual meeting of the Chemical Society of Japan on April 4, 1952.

* Excluding errors due to P_E and P_A.

Table 1

Dielectric constant and density increments of benzene solutions at 25°C.

	Compounds	Melting points	w $\times 10^5$	$\Delta\varepsilon$ $\times 10^3$	Δd $\times 10^4$
I	Bromotropolone	190°[ab]	429	12	15
			781	21	32
II	Bromotropolone	108°[ab]	329	26.3	10.8
			568	46.3	—
			1090	89.0	45.5
			1682	141.3	73.5
III	Dibromotropolone	161°[b]	227	15	8
			856	45	43
			1250	69	66
IV	Tribromohinokitiol	90.5°[c]	371	10	16
			836	21	41
			1057	29	52
V	α-Thujaplicin A	34°[d]	344	26.6	6.2
			657	49.8	11.1
			1023	77.9	18.3
VI	α-Thujaplicin B	25.5°[d]	347	26.7	7.9
			788	61.2	15.8
			1284	97.1	24.5
VII	Dibromo-α-thujaplicin	80–1°	309	8	13
			633	17	26
			1113	30	46

(a) T. Nozoe, S. Seto, Y. Kitahara, M. Kunori and Y. Nakayama, *Proc. Japan Acad.*, **26**, No. 7, 38 (1950).
(b) T. Nozoe, Y. Kitahara, K. Yamane and A. Yoshikoshi, ibid., **27**, 18 (1951).
(c) T. Nozoe, T. Mukai, K. Takase and A. Matsukuma, ibid., **27**, 152 (1951).
(d) T. Nozoe, Y. Kitahara, K. Yamane and T. Ikemi, ibid., **27**, 193 (1951).

Table 2

Molecular polarizations and dipole moments at 25°C.

	ε_1	d_1, g./cc.	α	β, g./cc.	P, cc.	R_D, cc.	μ, D
I	2.274	0.8709	2.56	0.483	128	40.3	2.07
II	2.2705	0.87069	8.48	0.463	354.2± 2.8	40.3	3.91±.02
III	2.2753	0.87100	5.23	0.566	309 ±14	48.1	3.57±.10
IV	2.2725	0.87117	2.72	0.525	260 ±16	69.6	3.05±.13
V	2.2730	0.87133	7.55	0.179	278.5± 2.0	46.3	3.37±.02
VI	2.2736	0.87153	7.51	0.177	279.6± 3.9	46.3	3.37±.03
VII	2.2726	0.87153	2.74	0.411	224.6± 1.7	61.9	2.82±.02

Discussion.—In order to determine the position of substituents in these molecules, we calculated the values of the moments for various possible isomers with the following assumptions. (1) The tropolone ring has a regular heptagon form. Hence the bond moments lie along the lines from the center of the ring to their respective carbon atoms. This assumption is supported by an electron diffraction experiment by Heilbronner and Hedberg[8] and that carried out in our laboratory.[9] (2) The bond moment was assumed to have the same value as in the corresponding benzene derivative, i. e., μ(C-Br)=1.5 D, μ(C-i-C_3H_7)=−0.65 D, μ(C-NO_2)=4.0 D. (3) The substitution by electrophilic atoms and groups such as bromine and nitro-group are most liable to take place at carbon atoms 3(ortho), 5(para) and 7 (ortho′). This was derived from our molecular orbital treatment[2] and is in conformity with the results in organic synthesis.* (4) The moment of tropolone, 3.5 D** in magnitude, lies along a line pointing from the center of the ring to the middle point of two oxygen atoms with its positive end at the ring. That this assumption holds approximately is supported by our previous conclusion from dipole moment measurement.[1] The calculated moments were compared with the experimental data and the position of substituents was determined as shown in Table 3.

Table 3

The position of substituents in tropolone derivatives

Compounds	μobs	μcalc	Position of substituents
Bromotropolone	2.07	2.00	5 or p
Bromotropolone	3.91	4.10	3 or o
Dibromotropolone	3.57	4.16	3,7 or oo'
Tribromohinokitiol	3.05	3.10	3,5,7 or $oo'p$
α-Thujaplicin A	3.37	3.42	3 or o
α-Thujaplicin B	3.37	3.42	3 or o
Dibromo-α-thujaplicin	2.82	3.03	5,7 or po'

In general the agreement between the observed and the calculated moments is good, considering the approximations made in the calculation. The slight discrepancy in the case of oo'-dibromotropolone may be due to the strong steric and induction effects between oxygen and bromine atoms, as was also the case in oo'-dibromohinokitiol.[3] In tribromohinokitiol, the agreement is as good

(8) E. Heilbronner and K. Hedberg, *J. Am. Chem. Soc.*, **73**, 1386 (1951).
(9) M. Kimura and M. Kubo, This Bulletin, **26**, 250 (1953).
* Cf. reference (a) and (b) of Table 1.
** Recalculated using Halverstadt-Kumler's method.

as can be expected, while such was not the case in tribromotropolone.[1] We recalculated the moment for the latter using the Halverstadt-Kumler's method instead of graphical extrapolation and obtained the moment value 2.46 *D*, which is close to the theoretical value of 2.66 *D*. Hence we can conclude that the successive substitution by bromine in tropolone or hinokitiol do not affect the structure or the electronic state of tropolone ring, though Hazato[4] reported the peculiarity of tribromotropolone. Our conclusion is in conformity with Kimura's result on electron diffraction that in tribromotropolone the structure of tropolone ring is nearly identical with that of tropolone.[9]

In view of the fact that the Halverstadt-Kumler's method gives better results than the ambiguous graphical extrapolation, we have recalculated the data on α-dinitrohinokitiol (m. p. 155°),[1] for which we could not get a definite conclusion. The observed value recalculated is 4.79 *D* and this is in good agreement with the theoretical value of 4.5 *D* for 5,7(or *po'*)-dinitrohinokitiol. This assignment can explain the results in organic synthesis[10] adequately.

The two crystal forms of α-thujaplicin gave an identical moment. The conceivable two molecular forms of α-thujaplicin, i. e., 3-isopropylcycloheptatriene-2,4,6-ol-2-one-1 and 3-isopropylcycloheptatriene-2,4,6-ol-1-one-2 are expected to have values for their moments different from each other by an amount of about 0.4 *D* due to the induction effect. This should surely be detectable by experiment. The absence of such a difference indicates that the two crystal forms give identical molecules in solution. Probably the molecules in the two crystal forms are the same with each other, the difference being attributable to the arrangement of molecules in crystals.

(10) T. Nozoe, Y. Kitahara, K. Yamane and K. Yamaki, *Proc. Japan Acad.*, **26**, 14 (1950).

Summary

The dipole moments of seven tropolone derivatives were measured in benzene solution at 25°C. The values obtained are: bromotropolone (m. p. 190°C., 5-bromo-), 2.07 *D*; bromotropolone (108°C., 3-bromo-), 3.91 *D*; tribromohinokitiol (90.5°C., 3,5,7-tribromo-), 3.05 *D*; α-thujaplicins, both A (34°C.) and B (25.5°C.) form, 3.37 *D*; dibromo-α-thujaplicin (80°C., 5,7-dibromo-), 2.82 *D*. By analysing the results obtained, the position of substituents in these molecules were determined and are given immediately after each name of these compounds in parentheses. The two crystal forms of α-thujaplicin with different melting points give an identical moment in solution. α-Dinitrohinokitiol of m. p. 155°C. is 5,7 (or *po'*)-dinitrohinokitiol.

We wish to express our thanks to Mr. T. Mizuno for his help in our experiment. Our thanks are also due to the Ministry of Education in aid of this research.

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Magnetic Susceptibilities of Reduced and Oxygenated Hemerythrins

By Masaji KUBO

(Received November 13, 1952)

The molecular weight of hemerythrin, an iron-containing respiratory pigment, determined by Adair's osmotic pressure method is 66,000.[1] Since hemerythrin contains 1.01% of iron, one molecule of hemerythrin contains twelve iron atoms. The molecule combines with oxygen in the proportion of one oxygen molecule to three atoms of iron,[2] hence the number of oxygen molecules fully combined with a hemerythrin molecule is four. This seems to be very peculiar in view of the fact that in two other iron-containing respiratory pigments, hemoglobin and chlorocruorin, the number of iron atoms in a molecule is equal to the number of oxygen molecules which can combine with it. To elucidate the problem more closely, I have undertaken magnetic susceptibility measurements on hemerythrin. Similar measurements, adopted by Pauling and

(1) A. Roche and J. Roche, *Bull. soc. chim. biol.*, **17**, 1494 (1935).
(2) M. Florkin, *Arch. intern. physiol.*, **36**, 247*(1933).

Coryell,[3] have led to a great extension of the structural knowledge of hemoglobin and related compounds.

Apparatus.—For the determination of magnetic susceptibility, a simple Gouy magnetic balance was employed. A test tube, filled with solution to a definite level, was suspended from a balance between the poles of a magnet. The test tube was 25 cm. long and 8.9 mm. in outer diameter, and the magnetic pole pieces were 7.2 cm. in vertical length and separated by 1.2 cm. The liquid meniscus was at the center of a strong homogeneous field of intensity H. The top and bottom ends of the tube were in a region of weak field H'. The current through the coil of the electromagnet was adjusted exactly to 9.7 amp; with this current magnetic saturation was almost attained. H and H' amounted to 1.03×10^4 and 2.2×10^2 oersteds respectively, hence H'^2 is entirely negligible compared with H^2. The effect of the residual magnetic field after the current was switched off was also small and need not be considered.

The magnitude of downward force f experienced by the tube along its length is given by the expression,

$$f=\frac{1}{2}(\kappa_{\text{gas}}-\kappa_{\text{liq}})H^2A=g\Delta w.$$

where κ_{gas}, κ_{liq} are the volume susceptibilities of the gas and liquid in the tube, A is the cross-sectional area of the liquid column having the value of $\pi(6.9/2)^2$ mm.^{2}, g the gravitational constant, and Δw the apparent increase in weight of the tube on application of the magnetic field.

The magnetic balance was operated at room temperature (25°), and was calibrated with distilled water saturated with air and its magnetic susceptibility per unit volume was set equal to -0.719×10^{-6}. The susceptibility per unit volume of the solution under investigation was calculated from

$$\frac{\kappa_{\text{gas}}-\kappa_{\text{sol}}}{\kappa_{\text{air}}-\kappa_{\text{water}}}=\frac{\Delta w_{\text{sol}}}{\Delta w_{\text{water}}}$$

To fill the upper part of the tube, 99.9% pure commercial nitrogen was used for reduced hemerythrin and air for oxygenated hemerythrin and water. It would be more desirable to use nitrogen in place of air to saturate the water and to remove dissolved oxygen completely from it. However, we had to use air for oxygenated hemerythrin and hence the effect of dissolved air is worth our attention. On the assumption of the additivity of magnetic susceptibility, the increase of susceptibility due to the paramagnetic contribution of dissolved oxygen can be calculated from the known solubility of the gas in water and the molecular susceptibility of oxygen, with the aid of Curie's law. The correction amounted to $+0.0009\times10^{-6}$, which is entirely negligible in comparison to -0.719×10^{-6} of pure water. It was of course ascertained that no bubbles of air came out of water or solution on the wall of the container during measurement. The value of π_{gas} is -0.00040×10^{-6} for nitrogen, which is entirely negligible compared with κ_{sol}, and $+0.0294\times10^{-6}$ for air. Two calibrated test tubes were used; one for reduced hemerythrin and the other for the oxygenated preparation in order to carry out the magnetic measurements at the same time.

Material.—The oxygenated hemerythrin solution was prepared as described in the preceding paper.[4] All the measurements on magnetic susceptibility, optical density, density, and the chemical analysis of iron were made on one and the same solution. These measurements were made in one day, except the iron analysis which took a longer time. The blood cells were washed during the previous evening and allowed to hemolyse overnight. One test tube for magnetic measurement was filled with approximately 5 cc. of the solution. Another part of the solution was deoxygenated in a tonometer, to which a test tube was attached by means of a rubber tube, according to the procedure already given.[4] After deoxygenation was complete, a portion of the solution was transferred to the test tube which was filled to the desired level for the magnetic measurements. The rubber tube was clamped on and a rubber stopper was inserted through the rubber tube to seal the test tube. In this case a very small quantity of air remaining in the rubber tube between the clamped part and the stopper was driven out by a stream of nitrogen injected through the rubber wall by means of a syringe and hypodermic needle.

It was of prime importance in this experiment that the concentration of deoxygenated and oxygenated solutions remained equal in spite of the repeated partial evacuation with an aspirator and equilibration with water-saturated nitrogen. To determine whether appreciable loss of water occurred, measurements were made on the optical density of the original oxygenated solution D_{ox}, that of deoxygenated solution D_{red}, and that of the latter solution exposed to and equilibrated with atmospheric air D'_{ox}. $D_{\text{ox}}-D_{\text{red}}$ and $D'_{\text{ox}}-D_{\text{red}}$ agreed with each other within 0.8%. Incidentally, this can be used to convert the relative concentrations in terms of optical density given in the previous paper into concentrations in terms of the iron content. The specific gravity of the solution at room temperature (25°) was found to be 1.018.

Determination of Iron Content.—The solution (16.408 g.) was dried in air at 100° (dry protein: 0.0221 g. per cc. of solution), and the iron content was determined by the thiocyanate method. A Coleman spectrophotometer was used for color comparison with green light of wave-length

(3) L. Pauling and C. D. Coryell, *Proc. Natl. Acad. Sci. U. S.*, **22**, 210 (1936); C. D. Coryell and F. Stitt, *J. Am. Chem. Soc.*, **62**, 2942 (1940).

(4) M. Kubo, This Bulletin, **26**, 189 (1953).

525 mμ. The concentration of the solution was found to be 7.88×10^{-6} g. atoms of iron per cc.

Results and Discussion

The results of magnetic measurements are summarized in Table 1. The susceptibility of reduced hemerythrin solution is higher while

Table 1

Magnetic Susceptibilities of Reduced and Oxygenated Hemerythrin Solutions at 25°.

	Δw(mg.)	Δw_{water}(mg.)*	$\kappa\times10^6$
Reduced	11.9	16.4	−0.543
Oxygenated	16.35	16.1	−0.731

* Two values do not agree with each other exactly, because different test tubes were used for them.

that of the oxygenated solution a little lower than that of water. It is obvious that although masked by the diamagnetic effect of the solvent and the protein part of hemerythrin, paramagnetic contribution attributable to iron is surely present in the reduced state, whereas such contribution is doubtful in oxygenated solution. The difference of molecular susceptibilities of reduced and oxygenated hemerythrin molecules is given by

$$\chi_{red}-\chi_{ox}=12\times\frac{-0.543+0.731}{7.88}=0.286\,\text{cm.}^3,$$

in which the factor 12 is introduced to take account of the fact that one molecule of hemerythrin contains twelve iron atoms. The difference method is particularly elegant because of the automatic cancellation of the effect of minute quantities of impurities such as indifferent proteins and sodium chloride, which might have come from blood cells and the solution used to wash them respectively, and of the diamagnetic term χ_0 in

$$\chi=\chi_0+N\frac{\mu^2}{3kT}$$

where μ denotes magnetic moment and other notations have their usual significances.

The change in magnetic susceptibility is, to be sure, closely connected with an iron atom or atoms directly combined with oxygen and those affected by it. In a complex molecule such as hemerythrin containing many iron atoms, there is a certain ambiguity as to the interpretation of μ. Let us assume that the different magnetic groups acting at the same time as oxygen-combining centers are oriented entirely independently of one another in the external magnetic field, as if located in separate molecules. This assumption will be justified, since as revealed by the studies on oxygen equilibrium[4] the mutual interaction between these centers is weaker, indicating greater distance between them, than in the case of hemoglobin, for which Pauling and Coryell[5] have given ample reasons for believing that the different magnetic groups in the molecule are magnetostatically independent. The further assumption will be made that the four groups in question are equivalent. Otherwise we would have obtained a more complicated shape of the oxygen equilibrium curve. Then we have

$$\chi_{red}-\chi_{ox}=\frac{4N}{3kT}\left(\mu^{*2}_{red}-\mu^{*2}_{ox}\right)$$

in which μ^* denotes the magnetic moment of each group acting as an oxygen combining center. Quantum mechanical considerations give for a magnetic moment

$$\mu^2=g^2\beta^2J(J+1)$$

where g is the gyromagnetic ratio, β is the Bohr magneton, $eh/4\pi mc$ in Gaussian units, the numerical value of which is 9.2726×10^{-21} erg gauss^{-1} or erg$^{1/2}$ cm.$^{3/2}$, and J the resultant angular momentum in units $h/2\pi$. Neglecting contributions due to orbital moments, and putting $g=2$ and $J=n/2$ for electrons, where n denotes the number of unpaired electrons, we have

$$\mu=\sqrt{n(n+2)}\beta$$

for the effective moment. In connection with the assumption that the spins only are involved, it will be worthwhile to point out that the orbital moments are appreciable for rare earth elements but are probably not very large for other transition group elements.[6] μ in this general treatment corresponds μ^* in this particular problem of a complex molecule. Hence

$$\chi_{red}-\chi_{ox}=\frac{4N\beta^2}{3kT}\left[n(n+2)_{red}-n(n+2)_{ox}\right]$$

Putting numerical values in the equation, we have

$$n(n+2)_{red}-n(n+2)_{ox}=171$$

There is no ad hoc reason to assign any particular value to n_{red} or n_{ox}. The assumption

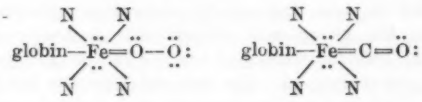
(5) L. Pauling and C. D. Coryell, *Proc. Natl. Acad. Sci. U. S.*, **22**, 159, 210 (1936).

(6) Cf. for example P. W. Selwood, Magnetochemistry, Interscience Publ. Inc., New York, 1943, p. 144.

that the oxygenated group has no unpaired electrons, $n_{ox}=0$, will give for the number of unpaired electrons in the deoxygenated group the value of 12.1 per three atoms of iron, which fixes the lower limit of n_{red}. This fact can hardly be explained if we suppose that only four of the twelve iron atoms of a hemerythrin molecule play a role in combining with four oxygen molecules and that other eight iron atoms remain indifferent. It is known that the iron in hemerythrin is in the ferrous state and that if it is oxidized to the ferric state, the resulting methemerythrin has a brownish color which no longer disappears when its solution is subjected to a vacuum or to the action of a reducing agent.[7] In an isolated ferrous ion or in a hydrated ferrous complex ion $[Fe(OH_2)_6]^{++}$, in which the bonds between the iron atoms and water molecules are essentially ionic or the ion-dipole type, the six outer electrons in excess of those required to form a completed argon shell occupy five $3d$ orbitals, and give rise to a normal state in which four of the electron spins are unpaired. In a covalent ferrous complex ion such as $[Fe(CN)_6]^{-IV}$, on the other hand, the six outer electrons of iron occupy three $3d$ orbitals with their spins paired, the other two $3d$ orbitals forming octahedral bond orbitals with one $4s$ and three $4p$ orbitals, resulting in no unpaired electrons. Therefore irrespective of whether the bonds of iron atoms are ionic or covalent it is very improbable that three ferrous iron atoms contained in a reduced hemerythrin group can have more than twelve unpaired electrons. Hence we can conclude that the number of unpaired electrons in a group acting as an oxygen combining center in reduced state, n_{red}, is twelve.

The calculated value of n_{red} is rather insensitive to the assumed value of n_{ox} so long as the latter is less than three, the calculated value of n_{red} being 12.1$\sim$12.4 for the assumed value of n_{ox} ranging from 0 to 2. Hence we have no means to decide from experimental data alone which of the three values $n_{ox}=0$, 1, 2 is correct. In fact the neglect of orbital contributions to the moment overestimates the number of unpaired electrons, while the assumption of complete coupling between different iron atoms in a group underestimates the number. Theoretically $n_{ox}=1$ or 2 is improbable and the most probable one among these three values will be $n_{ox}=0$.

Reduced hemerythrin, like ferrohemoglobin, must therefore be regarded as containing an ionic type of bonding of all iron atoms, whereas in oxygenated hemerythrin all the bonds are essentially covalent in nature. It is a very remarkable fact that oxygen molecules combining with the pigment molecule exert such a profound influence on the electronic structure of all iron atoms present. Pauling and Coryell[8] suggest as the most probable linkage of an oxygen molecule or carbon monoxide molecule coordinated with an iron atom in hemoglobin the following formulas:



resonating between other possible electronic structures. In this connection it is important to point out that the similarity of hemerythrin and hemoglobin lies in their physiological function as oxygen-transporters rather than in their chemical properties. Unlike hemoglobin, hemerythrin does not combine with carbon monoxide. In fact Florkin[9] found that hemerythrin combined with the same amount of oxygen whether the partial pressure of carbon monoxide was 4 or 150 mm. Hg., and Roche[10] found that bubbling carbon monoxide through a hemerythrin solution brought about no change in its spectrum. This fact makes it very likely that the combination of oxygen with hemerythrin takes place in a quite different manner from that of oxygen with hemoglobin. At present our knowledge on the structure of hemerythrin molecule is so limited that it is almost impossible to propose any definite idea to explain how an oxygen molecule can affect the electronic states of all the three iron atoms in the group. Possibly these iron atoms are coupled with each other in a polynuclear complex so as to be able to transmit the effect of the change of electronic state directly to others. We may have in the diamagnetic state of oxygenated hemerythrin a situation similar to that in certain polynuclear complexes such as iron enneacarbonyl, in which two iron atoms, with an odd number of electrons, coexist in the same molecule, and yet the molecule is diagmagnetic. A possible explanation is that there is some kind of electron pairing taking place, because of the proximity of the iron atoms to one another.

(7) G. F. Marrian, *Brit. J. Exptl. Biol.*, **4**, 357 (1927); M. Florkin, loc. cit.; J. Roche, *Bull. soc. chim. biol.*, **15**, 1415 (1933).

(8) L. Pauling and C. D. Coryell, loc. cit.

(9) M. Florkin, loc. cit.

(10) J. Roche, loc. cit.

Summary

The magnetic susceptibilities of reduced and oxygenated hemerythrin solutions of the same concentration were measured by a Gouy magnetic balance at 25°. The susceptibility of the reduced solution was found to be higher than that of the oxygenated one, indicating a paramagnetic contribution of iron atoms in the reduced molecule. With the assumptions that the four groups acting as oxygen combining centers in the molecule are equivalent to one another and that they are magnetostatically independent, the number of unpaired electrons in the group was calculated to be twelve in the reduced state and zero in the oxygenated preparation. In the reduced state the bonds of the iron atoms are ionic or ion-dipole type in nature. A profound change in the electronic structure takes place when oxygen molecules are combined with the hemerythrin molecule. An oxygen molecule not only loses its own paramagnetism, but also affects all three iron atoms in the group in such a way that the bond type is essentially covalent. These iron atoms are supposed to be coupled with each other in a polynuclear complex so as to be able to transmit the effect of the change of electronic state directly to the others.

The present experiments were made at the Biological Laboratories, Harvard University and the magnetic measurement at the Department of Metallurgy, Massachusetts Institute of Technology. I wish to express my sincere thanks to Prof. Jeffries Wyman, Jr. for his interest and suggestions and to Prof. Albert R. Kaufmann of MIT for giving me facilities to use his magnetic balance.

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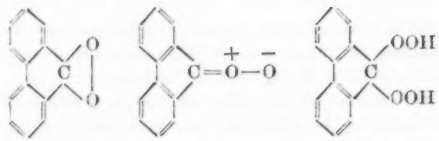
The Dipole Moments of Fluorenone Peroxide and Bishydroperoxide

By Keniti HIGASI

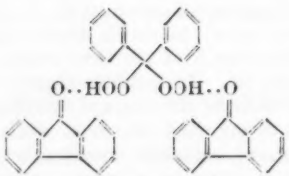
(Received November 19, 1952)

In 1940, Wittig and Pieper[1] prepared a new monomeric peroxide, viz., the so-called "fluorenone peroxide"[1] and discussed its structure. They regarded the formula (I) as unsatisfactory, because the yellow color of the crystal seemed to reveal a ketonic double bond. And they favored the oxo-ōxide structure (II) instead, which appeared to agree with many of its properties, including its solubilities.

In 1942, Prof. Murakami, of Osaka University, offered me this substance prepared by the Wittig and Pieper's method and we measured its dipole moment in benzene at room temperature. It was then evident from the observed value of its moment, viz., 3.1D that the ring structure (I) which has a smaller moment than 2D should be ruled out. Further, the oxo-ōxide structure which corresponds to a large moment of about 6D could not represent the actual state of the molecule. In the preceding article[2] it was suggested, therefore, that resonance occurs among various structures including (II), resulting in a lesser moment.



(I) (II) (III)



(IV)

(1) G. Wittig und G. Pieper, *Ber.*, **73**, 295 (1940).

(2) K. Higasi, *Bull. I. P. C. R. Tokyo*, **21**, 1147 (1942).

In 1949, Criegee, Schnorrenberg and Beck[3] reported that Wittig's "fluorenone peroxide" is not a simple substance but a mixture of two molecules of fluorenone and one molecule of its bishydroperoxide (III). In benzene solution this molecular compound (IV) dissociates into the three components, giving a monomeric value in the molecular weight determination.

In the present note I wish to report the result of a reexamination of our data from the view-point of Criegee and his pupils. From the apparent polarization of "fluorenone peroxide", the total polarization of the molecular compound (in a dissociated state) was calculated, and then by subtracting the polarizations of two fluorenone molecules,[4] the polarization of the bishydroperoxide (III) was obtained. The dipole moment thus evaluated for the latter substance was 2.4D* in benzene (with fluorenone).

The polarity of the bishydroperoxide (III) arises chiefly from the two C—O dipoles and two O—H dipoles. Besides these, there are small moments induced in the hydrocarbon residue, but a correction for them may be included in the resultant moment for C—O dipoles, which are in a fixed position to the plane of rings. In contrast to these, the two O—H dipoles can rotate around two axes of rotation, viz., the C—O, and O—O linkages (Fig. 1). As a first approximation we may regard the polarity of the molecule as consisting of three independently rotating dipoles, viz., one for O–C–O dipole of 1.0D, and the other two of 1.53D each for the O—H groups.[5] This rough picture was in fact in good accord with the observed moment, giving 2.38D as the calculated moment.**

Further, it is of interest to find that the apparent polarization of fluorenone peroxide increases with the increase in concentration, and that the bishydroperoxide reveals the same tendency but that it is even more pronounced. In Fig. 2 the molecular polarization of the bishydroperoxide was plotted against the mole fraction of the solute and compared with the curve for fluorenone itself.

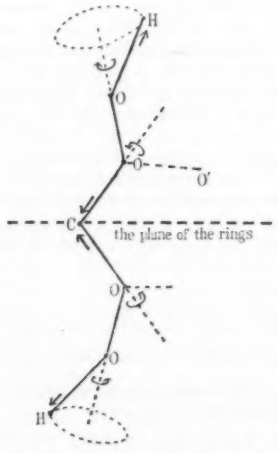


Fig. 1.—The axes of rotation in bishydroperoxide

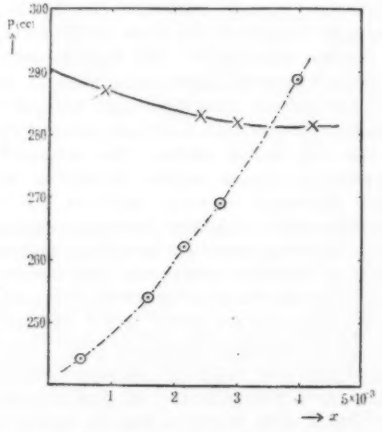


Fig. 2.—Molecular polarization in benzene solution at 25°C (P) and mole fraction (x).
× Fluorenone (Le Fèvre et al[4])
⊙ Bishydroperoxide (Higasi, the sample B*)

The increase in polarization with increasing concentration may be accounted for by making any of the following two assumptions. First, we regard it as characteristic of the solute with O—H group, e.g., the polarizations of alcohols in hexane. Secondly, the bishydroperoxide has a strong tendency to interact with one or two molecules of fluorenone, thus forming very polar complexes. The latter interpretation may be the more plausible,

(3) R. Criegee, W. Schnorrenberg and J. Beck, *Ann.*, **555**, 7 (1949).

(4) E. D. Hughes, C. G. Le Fèvre, R. J. W. Le Fèvre, *J. Chem. Soc.*, 207 (1937).

* The sample A (m. p. 107°~8°) gave 3.1D for fluorenone peroxide and 2.4 D for the bishydroperoxide, while the sample B (m. p. 104°) gave 3.2 D and 2.9 D, respectively. The sample A was recrystallized from B (Cf. Wittig and Pieper: m. p. 108°).

(5) C. P. Smyth, *J. Phys. Chem.* **41**, 209 (1937); and other papers.

** The moment of the bishydroperoxide m is calculated as $m^2=1\times1.0^2+2\times1.53^2$.

because the chance for the association in this type is twice that in the former.

In conclusion, it may be safely stated that a better explanation of our dielectric measurement can be obtained from the work of Criegee and his school than from that of Wittig and Pieper.

I wish to thank Professor M. Murakami of Osaka for the gift of materials and also Doctor R. K. Start of Obuse for his generous assistance in the preparation of the English manuscript.

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Electron Diffraction Investigation on Tropolone*

By Masao KIMURA and Masaji KUBO

(Received November 19, 1952)

We have already measured the dipole moments of tropolone and some of its derivatives in benzene solution.[1] The high moments of tropolone were explained adequately by taking into account the contribution of various resonance structures with a formal positive charge at the ring carbon atoms. The resonance was supposed to give a certain amount of double bond character to each bond in the ring, resulting in a coplanar heptagon configuration. The supposition was still too indirect to allow a definite conclusion and hence we undertook an electron diffraction experiment on tropolone to get more direct evidence in support of a regular heptagon ring. After the experiment was complete, an experiment similar to ours was published by Heilbronner and Hedberg[2] and X-ray study by Robertson[3] on the copper complex of tropolone. Though our results were essentially the same as those of Heilbronner and Hedberg, we think it worthwhile to report them in detail, because we could explain the appearance of a peak in the radial distribution function which they failed to assign to any possible distance, and in addition we could deal with the two C-O distances in more extensive manner, the results of which will be of much interest concerning the possible symmetry of this molecule.

Material and Experimental Method.—The tropolone sample (m. p. 50~51°) was synthesized and purified at the laboratory of organic chemistry, Tohoku University.[4] It was evaporated at a temperature several degrees higher than its melting point, and was led through a high temperature nozzle into a vacuum chamber to interfere with an electron beam of 0.05~6 A. wavelength calibrated with a gold foil. The diffraction photographs were prepared in the usual way.[5] The camera distance was 11 cm.

Experimental Results.—The visual intensity curve obtained is shown in Fig. 1 (V_1).* The q ($=10s/\pi$) values for the maxima and minima of diffraction halos are given in Table 1.

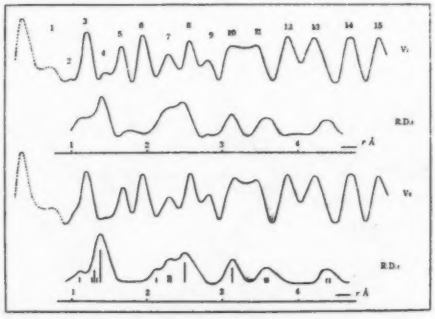

Fig. 1.—Visual curve and the radial distribution function of tropolone

* Read before the scientific meeting of the Chemical Society of Japan held on April 4, 1952.

(1) Y. Kurita, T. Nozoe and M. Kubo, This Bulletin **24**, 10, 99 (1951).

(2) E. Heilbronner and K. Hedberg, *J. Am. Chem. Soc.* **73**, 1386 (1951).

(3) J. M. Robertson, *J. Chem. Soc.*, **1951**, 1222.

(4) T. Nozoe, S. Seto, Y. Kitahara, M. Kunori and Y. Nakayama, *Proc. Japan Acad.*, **26**, (7) 38 (1950).

(5) M. Kimura, *Chemical Researches*, **9**, 53 (1951).

* The dotted portion was obtained from the theoretical intensity curve calculated for the molecular structure inferred from the preliminary radial distribution function, which was derived from the full line part of the visual intensity curve.

Table 1

The q values for the maxima and minima of diffraction halos

Max.	Min.	q	Max.	Min.	q
1		10.06		9	49.04
	2	12.10	9		51.59
2		14.68		10	54.23
	3	16.62	10		58.74
3		19.10		11	62.61
	4	21.78	11		65.18
4		24.10		12	68.20
	5	26.13	12		72.32
5		28.43		13	75.89
	6	31.04	13		79.60
6		33.91		14	85.00
	7	37.39	14		89.03
7		40.89		15	92.99
	8	43.70	15		96.51
8		46.47			

The radial distribution function,

$$rD(r) = \sum_{q=1}^{\max} I_q \exp(-aq^2) \sin\left(\frac{\pi}{10} qr\right)$$

calculated from the visual intensity curve V_1 is shown in Fig. 1 (RD_1). Here notations have their usual significances and the constant a was chosen so that $\exp(-aq^2)=0.1$ at $q_{\max}$. The peaks at 1.39 and 3.13 A. are sharp and hence the values are accurate. Those at 3.59 and 4.38 A. are distinct but broad, presumably due to the close proximity of two different distances.* The humps at 1.10, 2.30 and 2.48 A. are less distinct and are not suitable for obtaining accurate values for the distance. Of the three weak maxima at 1.75, 2.80 and 4.02 A., the latter two seem to be insignificant, while the first one corresponds evidently to the fairly conspicuous peak at 1.73 A. of Heilbronner and Hedberg. These peaks and humps can be explained properly except the three weak maxima as shown in Table 2 (3rd and 4th columns) with the following two assumptions. (1) The tropolone ring has a plane regular heptagon form shown in Fig. 2 with edges 1.39 A. long. (2) Each of the C-O bonds of 1.30 A. in length lie along a line bisecting the respective $\angle$CCC angle.

The C-O distance of 1.30 A., O-O distance of 2.52 A. and C-H distance of 2.13 A. will be masked respectively by peaks at 1.39, 2.51 and 2.28 A. The flat peak at 1.75 A. less obvious than that of Heilbronner and Hedberg does not correspond to any possible distance. We suspected that the appearance of this peak might be due to the inaccuracy of intensity estimation by visual method on the 1st, 2nd, 4th, 7th and 9th maxima. We therefore tried to modify the visual curve V_1 in such a way that the ghost disappears. The resulting curve and the radial distribution function obtained from it are shown in Fig. 1 (V_2 and RD_2). The three ghosts in question disappear in the radial distribution function. The curve V_2 is in conformity with the visual estimation except that here the 2nd and 4th weak maxima in V_1 appear as inflection points. It is very hard to determine accurately the intensity of such maxima by visual method. In fact it is known that a weak maximum observed by naked eyes, if examined by microphotometry on a diffraction photograph taken with a sector, turns out to be an inflection point of the curve. Hence we believe that V_2 rather than V_1 is nearer the truth and wish to point out that in view of the fact that the whole visual curve affects the radial distribution function, it is possible that small errors in visual curve may give rise to fortuitous maxima in radial distribution function. The interatomic distances from the modified radial distribution function RD_2 are given in the last column of Table 2. The agreement with the calculated values is excellent.*

In order to determine C-O distance which was masked by a very strong peak at 1.39 A. in the radial distribution function, we calculated the theoretical intensity curve

Table 2

Interatomic distances in tropolone

Bond	Ratio of Z_iZ_j/r_{ij}	Interatomic distance, A. calc.	obs. RD_1	obs. RD_2
C_1-C_2	18	1.39	1.39	1.39
C_1-C_3	11	2.51	2.48	2.51
C_1-C_4	8	3.12	3.13	3.13
O_1-C_2	8	2.28	2.30	2.32
C_1-O_1	7	1.30	—	—
O_1-C_3	5	3.61	3.59	3.60
O_1-C_4	4	4.40	4.38	4.39
O_1-O_2	3	2.52	—	—
C-H	3	1.10	1.10	1.10
C···H	3	2.13	—	2.13

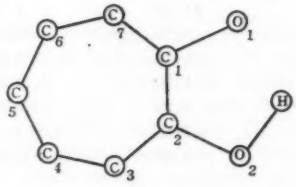

Fig. 2.

* Another explanation that this is due to the vibrational motion of atoms is less likely, because we should then expect similar broadening for the peak at 3.13 A as will be clear in later paragraphs.

* Vertical bars in Fig. 1 (RD_2) indicate distances calculated for the best model. The heights of the bar are drawn proportional to Z_iZ_j/r_{ij}.

$$I(q) = \sum_{i<j} \sum \frac{Z_i Z_j}{r_{ij}} \sin\left(\frac{\pi}{10} qr_{ij}\right)^*$$

for various values of C_1-O_1 and C_2-O_2 distances ranging from 1.18 to 1.38 A. Here Z_i and Z_j denote the atomic numbers of i- and j-atoms respectively and r_{ij} the distance between them. The ring was assumed to have a regular heptagon form with C-C distance equal to 1.39 A. The line along the C-O bond was assumed to bisect ∠CCC angle. The effect of hydrogen atom could be neglected. A part of the results are summarized in Table 3 and Fig. 3.

Table 3

Various models for the theoretical intensity curves

Model	C_1-O_1 distance, A.	C_2-O_2 distance. A.
1	1.26	1.26
2	1.30	1.30
3	1.34	1.34
4	1.22	1.30
5	1.22	1.38
6	1.26	1.34
7	1.30	1.38

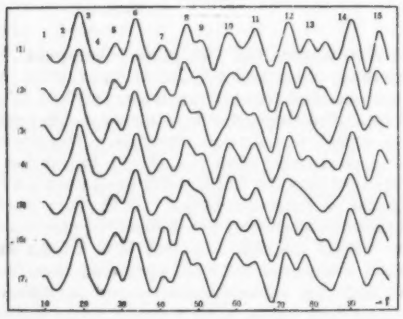

Fig. 3—Theoretical intensity curve

The following experimental facts will serve as a criterion to discard some of the presumed values of C-O distance. (1) The 10th and 11th maxima in the visual intensity curve with nearly equal intensity are broad. (2) The 12th and 13th maxima have nearly equal strength and are sharp. It was found that if the two C-O distances were assumed to have equal length (Cf. models 1~3), a distance of 1.26 as well as 1.34 A. does not fit the experiment. If the two C-O distances are different, we have naturally a variety of choice, though a distance less than 1.22 A. or greater than 1.40 A. (Cf. models 4 and 5) for one of the two C-O bonds does not give any theoretical intensity curve in agreement with the experiment. If we take vibrational motion into account, the theoretical intensity curve changes in such a way that both the 10th and the 11th maxima become a little flatter, the degree of change being greater for the former than for the latter and that the shelf at the lower right foot of the 13th maximum becomes less obvious. These changes, however, do not alter the conclusions derived for the fixed model. After closer examination,** we found that the best fit with experiment could be obtained for the model 6. The agreement of this model with experiment and the broad peak at 3.60 and 4.39 A. in the radial distribution function seem to imply that tropolone is a mobile tautomeric system of unsymmetrical molecules with the hydrogen atom not occupying a position midway between the two oxygen atoms. The unsymmetrical structure was also favored by Dewar,(6) Cook(7) and others(8) and by Nozoe.(9)

Summary

The molecular structure of tropolone was studied by the electron diffraction method. The most plausible model was found to be a plane regular heptagon form with C-C distance 1.39 A. long and C-H distance 1.10 A., having two slightly different C-O distances, i.e., C-O =1.34 A. and C=O=1.26 A.

We wish to express our thanks to Prof. Nozoe of Tohoku University for providing us with the material prepared for use in the present investigation and to Prof. Morino of Tokyo University for valuable discussions. Our thanks are also due to the Ministry of Education for grants in aid of this research.

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* The effect of vibration of atoms in the molecule, which is not taken into account in this equation, did not affect appreciably the position of maxima and minima and also the relative intensity of maxima lying close together. This will be explained in detail later.

** It was found that a deviation less than 5° of C-O directions in or out of the ring plane does not affect appreciably the theoretical intensity curve. The deviation of this direction greater than about 5° is unlikely, though it may afford another possibility of explanation for the broadness of peaks at 3.60 and 4.39 A.

(6) M. J. S. Dewar, *Nature*, **155**, 50, 141, 479 (1945).
(7) J. W. Cook, A. R. Gibbs, R. A. Raphael and A. R. Somerville, *J. Chem. Soc.*, **1951**, 503.
(8) H. P. Koch, ibid., **1951**, 512; G. P. Scott and D. S. Tarbell, *J. Am. Chem. Soc.*, **72**, 240 (1950).
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Antituberculous Compounds. II. Thiosemicarbazones from Benzalacetones[1]

By Tamio NISHIMURA

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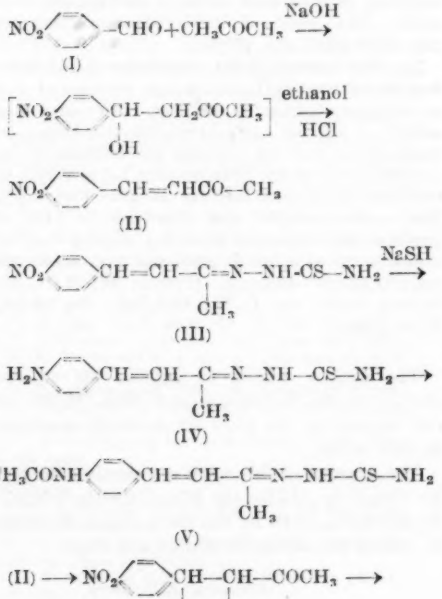
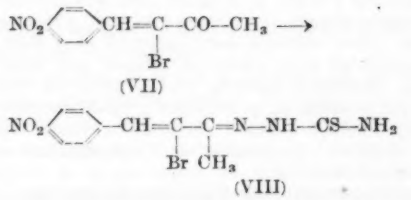
In a previous communication the author has reported the synthesis of *p*-acetamidocinnamaldehyde thiosemicarbazone as a vinylog of Tibion.[2] In our laboratory this thiosemicarbazone has been shown not to have antituberculous activity over that of Tibion in an *in vivo* test.[3] But in connection with this study, it would be interesting to compare the antituberculous activity of the thiosemicarbazones previously reported with that of other vinylogous thiosemicarbazones having similar structure. For this purpose the author synthesized *p*-acetylaminobenzalacetone thiosemicarbazone (V) and 1-(*p*-nitrophenyl)-2-bromo-1-butene-3-one thiosemicarbazone (VIII), according to the following scheme.



(1) A part of this study was presented at the annual meeting of the Chemical Society of Japan in Tokyo on April 5, 1952.
(2) T. Nishimura, This Bulletin, **25**, 54 (1952).
(3) K. Mizunoe, Unpublished data.



p-Nitrobenzaldehyde (I) was prepared from *p*-nitrotoluene as described before.[2] According to the method of Baeyer and Becker,[4] (I) was condensed with acetone and dehydrated to produce *p*-nitrobenzalacetone (II), without giving good results. However, it was found that the condensation reaction proceeded smoothly at room temperature when a mixture of acetone and water (1:1) was used. On condensation and dehydration, Baeyer and Becker's so called "*p*-nitrodicinnamyl methyl ketone"[4] was obtained in a considerable amount. The condensation product, 4-hydroxy-4-(*p*-nitrophenyl)-2-butanone was extracted with ether and dehydrated with hydrochloric acid without isolating it in a crystalline state. (II) was condensed with thiosemicarbazide in ethanol to give *p*-nitrobenzalacetone thiosemicarbazone (III) which was reduced to *p*-aminobenzalacetone thiosemicarbazone (IV) with sodium hydrogen sulfide. *p*-Acetamidobenzalacetone thiosemicarbazone (V) was obtained by acetylation of (IV) with acetic anhydride in ethanol.

1-(*p*-Nitrophenyl)-1, 2-dibromobutan-3-one (VI) was obtained by the action of bromine on (II) in glacial acetic acid, which was converted to 1-(*p*-nitrophenyl)-2-bromo-1-buten-3-one (VII) by dehydrobromination with potassium carbonate or pyridine.

Experimental[5]

***p*-Nitrobenzalacetone (II).**—A mixture of 30.2g. (0.2 mole) of *p*-nitrobenzaldehyde, 60 ml. of acetone and 60 ml. of water in a 300 ml. Erlenmeyer flask was made slightly alkaline by adding

(4) A. Baeyer and P. Becker, Ber. **16**, 1968 (1883).
(5) All temperatures are uncorrected.

4 drops of 10% sodium hydroxide solution. The mixture was shaken for 25 minutes at room temperature while *p*-nitrobenzaldehyde disappeared, yielding a small amount of undissolved "*p*-nitrodicinnamyl methy ketone." The reaction mixture was neutralized with 10% hydrochloric acid and extracted with 120 cc. and then 60 cc. of ether. The ether extracts were combined, filtered and concentrated on a water bath. The concentrated solution was mixed with 60 cc. of ethanol and 40 cc. of 10% hydrochloric acid, heated for 4 hours on a steam bath and allowed to stand overnight at room temperature. Precipitated yellow crystals were collected on a filter, recrystallized from 120 cc. of ethanol and dried in a desiccator, yielding 20.1 g. (53%) of the desired product, m. p. 107—108°. "*p*-Nitrodicinnamyl methyl ketone" (m.p. 244°) which did not dissolve in ethanol on recrystallization amounted to 6.7 g.

***p*-Nitrobenzalacetone thiosemicarbazone**(III).—Into a hot solution of 4.7 g. of thiosemicarbazide in 200 cc. of ethanol was added 9.6 g. of *p*-nitrobenzalacetone and the mixture was heated on a steam bath, giving 12.2 g. (92%) of the thiosemicarbazone, m. p. 240° (decomp.) (Found: N, 21.10% Calcd. for $C_{11}H_{12}O_2N_4S$: N, 21.21%).

***p*-Aminobenzalacetone thiosemicarbazone**(IV).—A mixture of 4 cc. of 2*N*-sodium hydroxide and 20 cc. of ethanol was saturated with hydrogen sulfide. To this solution was added 1.2 g. of *p*-nitrobenzalacetone thiosemicarbazone in one portion, and the mixture was refluxed for one hour. After cooling, the precipitated crystals were collected, washed with ethanol and water, yielding 0.9 g. (75%) of the desired product melting at 191° (decomp.). This material was dissolved in 7 cc. of pyridine and the solution was filtered. 7 cc. of water was added to the solution and it was allowed to stand overnight in an ice-box. Separated crystals were filtered and washed with ethanol and water, giving 0.8 g. of the same m. p. (Found: N, 23.93%, Calcd. for $C_{11}H_{14}N_4S$: N, 23.92%).

***p*-Acetylaminobenzalacetone thiosemicarbazone** (V).—A mixture of 0.6 g. of *p*-aminobenzalacetone thiosemicarbazone, 10 cc. of ethanol and 0.4 cc. of acetic anhydride was heated on a steam bath until complete dissolution took place. The solution was allowed to stand overnight at room temperature. Crystals were filtered and washed with ethanol and water, giving 0.5 g. (70%) of the desired product melting at 220—221°(decomp.). After recrystallization from 40 cc. of ethanol, there was obtained yellow plate melting at 223° (decomp.). Further recrystallization did not change the m. p. (Found: N, 20.12%. Calcd. for $C_{13}H_{16}ON_4S$: N, 20.28%).

1-(*p*-Nitrophenyl)-1,2-dibromobutane-3-one (VI).—3.2 g. of bromine was added with stirring to a solution of 3.8 g. of *p*-nitrobenzalacetone in 20 cc. of glacial acetic acid. The mixture was allowed to stand for two hours at room temperature and then overnight in an ice-box. Separated crystals were filtered and washed with ethanol and water to give 4.4 g. (63%) of the desired product melting at 118° (decomp.). The m. p. of a small sample recrystallized from glacial acetic acid (or ethanol) was 128° (decomp.) (Found: C, 34.69; H, 2.96; Br, 45.33%. Calcd. for $C_{10}H_9O_3NBr_2$: C, 34.21; H, 2.58; Br, 45.54%).

1-(*p*-Nitrophenyl)-2-bromo-1-buten-3-one (VII).—(a) A solution of 1.8 g. of 1-(4-nitrophenyl)-1,2-dibromobutane-3-one in 5 cc. of pyridine was heated for five minutes on a steam bath, followed by addition of 5 cc. of water. After cooling, 1.2 g. (89%) of the desired product melting at 119—120° was obtained. Recrystallization from ethanol gave the pure material melting at 120—121° (Found: C, 44.68; H, 3.28; N, 5.28% Calcd. for $C_{10}H_8O_3NBr$: C, 44.46; H, 2.99; N, 5.19%).

(b) 0.8 g. of bromine was added to a solution of 0.9 g. of 4-nitrobenzalacetone in 5 cc. of glacial acetic acid and the mixture was allowed to stand for 15 minutes. This was followed by the addition of 0.4 g. of anhydrous potassium carbonate. When the evolution of gas had ceased, the mixture was heated on a steam bath for 30 minutes and then 2 ml. of water added. On cooling, resulting crystals were collected and washed with water. The yield of the product melting at 118—119° was 1.0 g. (77%).

1-(*p*-Nitrophenyl)-2-bromo-1-buten-3-one thiosemicarbazone (VIII).—To a hot solution of 0.5 g. of thiosemicarbazide in 25 cc. of ethanol was added 1.4 g. of 1-(*p*-nitrophenyl)-2-bromo-1-buten-3-one and the mixture was refluxed for 20 minutes on a steam bath to give 1.3 g. (75%) of the desired product melting at 182° (decomp.). The crude material was dissolved in 7 cc. of pyridine and reprecipi tated by adding 5 cc. of water to the solution to yield the pure substance melting at 191° (decomp.) (Found: Br, 23.05; N, 16.59% Calcd. for $C_{11}H_{11}O_2N_4BrS$: Br, 23.29; N, 16.32%).

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Determination of Small Quantity of Pentosan in Cellulosic Materials

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I. Introduction

It is well known, that the phloroglucin method gives high values of pentosan content, on account of oxymethyl furfural produced from hexosan by acid distillation. In the case of chemical pulps especially high α pulps for cellulose ester or rayon tire cords, the apparent pentosan from hexosan becomes several times the true value and results in inaccuracy. Therefore, many methods have been advised to reduce or remove the influence of hexosan.

1) Barbituric acid method[1][2]

2) Decomposition of oxymethyl furfural by redistillation[3][4]

3) Dissolving oxymethyl furfural-phloroglucide by treatment with alcohol[3][5]

4) Colorimetry[6]~[9]

5) Determination utilizing the difference of the rates of thermal decomposition between furfural and oxymethyl furfural[10][11]

The method 1) gives lower values because of the solubility of the condensate in hydrochloric acid solution. As to the method 2), oxymethyl furfural is not only incompletely removed but also furfural is decomposed considerably. As for the method 3), the difference between the decomposition rates of oxymethyl furfural and furfural was smaller than expected and a good result was not obtained.

The method 3) is not a perfect one, but in Japan, phloroglucin method is predominantly adopted. So it is not useless to investigate the method more thoroughly. Colorimetric method 4) is promising as it is claimed that the influence of hexosan is under 0.1%. Then in this research, both the treatment of the phloroglucide with ethanol and the colorimetric method were investigated and the results were compared with barbituric acid, bromate and the usual phloroglucin methods, with special attention to the influence of hexosan on pentosan determination.

II. Improvement of Phloroglucin Method

1) **Experimental Procedures.**—The amounts of furfural and oxymethyl furfural produced by acid distillation, depend on the weight of the sample, distillation apparatus, variety and concentration of the acid, and rate and time of distillation. So, at first, these conditions were determined as follows:

The sample was weighed into a distillation flask (300 cc.) and 100 cc. of 12% hydrochloric acid solution was added and the mixture was heated in an oil bath. The temperature of the bath was regulated to obtain 30 cc. of the distillate in ten minutes and this was about 170°C. During the course of distillation, when every 30 cc. of the distillate was obtained, 30 cc. of 12% hydrochloric acid solution was tapped into the flask. To the total distillate (360 cc.), 40 cc. of phloroglucin-12% hydrochloric acid solution (7.33 g./l.) was added and the solution was kept standing for sixteen hours at 20°C. The phloroglucide was filtered on a glass filter 1G4, then 60 cc. of 95% ethanol was added to the precipitate in the glass filter and the mixture was kept standing for ten minutes at 60°C. The alcohol-insoluble residue was filtered on the glass filter and this procedure was repeated three times. In some cases, the initial phloroglucide was once dried at 105°C. and then treated with alcohol. Solubility in alcohol was calculated from the amount of phloroglucide before and after the alcohol-treatment and the portion dissolved in the mother liquor (hydrochloric acid solution) was

(1) E. Unger and R. Jäger, *Ber.*, **36**, 1222 (1903).
(2) S. Takehara, *J. Soc. Chem. Ind., Japan*, **47**, 74 (1944).
(3) K. Oshima and K. Kondo, *J. Coll. Agr. Hokkaido Imp. Univ.*, **16**, 52 (1926).
(4) C. Kullgren and H. Tydén *Cellulosechemie*, **11**, 15 (1930).
(5) T. Fukai and W. Nakajima, *J. Soc. Brewing, Japan*, **23**, No. 9, 18, No. 10, 18 (1928).
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(13) S. Takehara, *J. Soc. Chem. Ind., Japan*, **46**, 449 (1943).
(14) M. Hamada and I. Takano, *J. Agr. Dep. Kyushu Imp. Univ.*, **9**, No. 1 (1940).
(15) W. Gierisch, *Cellulosechemie*, **6**, 61, 81 (1925).

not considered. For calculation of xylose or pentosan content, the dissolved portion of the phloroglucide was assumed 5.2 mg. in 400 cc. of the mother liquor, even when the alcohol treatments were made.

2) **Experimental Results.**—(a) **Influence of times of the alcohol treatment.**—By means of one treatment, alcohol-soluble part was largely removed and completely eliminated by the operations of three times as shown in Table 1.

Table 1

Effect of Times of Alcohol-Treatment on Solubility in Alcohol

Glucose (g.)	3.0108	3.0091
Total phloroglucide (g.)	0.0320	0.0329
Alcohol-insoluble phloroglucide (g.)		
Time of treatment		
1	0.0142	0.0154
2	0.0137	0.0148
3	0.0137	0.0149
4	0.0138	0.0147
5	0.0139	0.0147

(b) **Apparent pentosan content from glucose, xylose and arabinose.**—According to Kröber, conversion ratios of xylose and arabinose to furfural were 88% and 73% respectively. He constructed his table in supposition that the pentosan in wood is a mixture of an equal amount of xylose and arabinose. Our experiment showed that these values were 86% and 72% respectively, and glucose also yielded phloroglucide which corresponded to 1.9% pentosan when calculated from Kröber's table. When the fresh, wet phloroglucides were treated with ethanol, 82% of the one from glucose was dissolved in ethanol but also 10~11% of those from xylose and arabinose were dissolved. After the precipitate was once dried, the alcohol-soluble portion was considerably lowered as shown in Tables 2 and 3. In the tables each experiment was duplicated and averaged.

(c) **Influence of the amount of phloroglucin added, on the alcohol-soluble portion.**—The

Table 2

Apparent Pentosan from Glucose (3.000 g.)

Condition of phloroglucide treated with alc.		Phloroglucide, mg.	Apparent pentosan, %*	Solubility, %
dry	before alc.	59.2	1.90	60.3
	after alc.	23.5	0.86	
wet	before alc.	—	—	82.1
	after alc.	10.6	0.47	

* Based on the weight of glucose and calculated from Kröber's table.

Table 3

Conversion ratios of Xylose and Arabinose to Furfural (sample, each 0.100 g., and the ratios were calculated from the amount of phloroglucide)

	Condition of phloroglucide treated with alc.		Phloroglucide, mg.	Conversion ratio, %	Solubility, %
Xylose	dry	before alc.	101.6	86.1	4.0
		after alc.	97.5	82.8	
	wet	before alc.	—	—	10.8
		after alc.	90.6	77.3	
Arabinose	dry	before alc.	84.0	71.9	1.5
		after alc.	82.7	70.9	
	wet	before alc.	—	—	10.0
		after alc.	75.6	65.2	

previous experiment showed that both the furfural- and oxymethyl furfural phloroglucide were divided into two parts, alcohol-soluble and -insoluble. It is clear that the cause is not the solubility of the precipitate in alcohol, such as in low-molecular weight compounds. Because the weight of the dissolved portion reached a constant value as the treatments were repeated.

Goodwin and Tollens[16] observed that, at room temperature, one mole of furfural condensed with one mole of phloroglucin under separation of one mole of water, but at 80°C. the precipitate was formed under dehydration of three moles of water. This indicates the oomposition of the phloroglucide is not constant and it is probable that this variation in composition would have effects on the solubility in alcohol. Then various amounts of phloroglucin were added to furfural and oxymethyl furfural solution, and the solubilities in alcohol of the phloroglucides produced were determined. 1 g. of furfural, purified twice by vacuum distillation, was dissolved in 1 l. of 12% hydrochloric acid solution, of which 10 cc., 30 cc., 50 cc. and 100 cc. were taken out and each was diluted to 360 cc. with 12% hydrochloric acid solution. To these solutions, the phloroglucin solution was added so as to make molar ratio of furfural to phloroglucin 1 : 2, 1 : 3, 1 : 5 and 1 : 10 and each was diluted with 12% hydrochloric acid solution to make the total volume 400 cc., The weights of the phloroglucides and their solubilities in alcohol were tabulated in Table 4. The solubilities were determined on the undried, wet samples, that were the same in the following experiments.

The table shows that the greater the ratio of phloroglucin to furfural, the larger is the solubility in alcohol of the precipitate. The amount of the phloroglucide (including alcohol-soluble part) always agreed well with the calculated value from the assumption that one mole of furfural condensed with one mole of phloroglucin under dehydration of two moles of water.

(16) W. C. Goodwin and B. Tollens, *Ber.*, **37**, 315 (1904).

Table 4

Effect of Phloroglucin added on the Solubility of Furfural-Phloroglucide in Alcohol

Furfural : Phloroglucin	Furfural Phloroglucide, theoretical / Phloroglucide, observed, %*	10 mg. 19.4 mg.	30 mg. 58.1 mg.	50 mg. 96.9 mg.	100 mg. 193.8 mg.
1 : 2	without alc.	93.8	100.3	99.1	—
	with alc.	69.5	88.6	91.1	95.5
1 : 3	without alc.	95.4	99.9	99.5	—
	with alc.	66.9	83.0	88.2	94.1
1 : 5	without alc.	93.8	100.6	99.9	—
	with alc.	54.1	78.3	84.9	91.7
1 : 10	without alc.	97.9	100.0	99.5	—
	with alc.	68.5	76.2	82.6	—

* Based on the theoretical amount.

Table 5

Effect of Phloroglucin added on the Solubility of Oxymethyl Furfural-Phloroglucied in Alcohol

Phloroglucin added*	Phloroglucide, observed, mg.		Apparent pentosan, %
1 : 2	without alc.	63.0	2.0
	with alc.	11.5	0.5
1 : 3	without alc.	63.3	2.0
	with alc.	10.8	0.5
1 : 5	without alc.	60.3	1.9
	with alc.	10.3	0.5
1 : 10	without alc.	60.9	2.0
	with alc.	11.0	0.5

* Based on apparent pentosan, 2% of the sample (glucose, 3.000 g.)

Next, similar procedures were applied to the oxymethyl furfural obtained from glucose by distillation with hydrochloric acid solution. From Table 5, it seems that neither the amount of phloroglucide nor its solubility in alcohol are influenced by the amount of phloroglucin added. But the color of the precipitate varied from brown to yellowish brown as the added amount was increased. This would indicate the composition of the phloroglucide varied according to the ratio of phloroglucin to oxymethyl furfural but its influence is not remarkable as the amount of the precipitate is small.

From the fact that the solubility of furfural-phloroglucide in alcohol increased with the amount of phloroglucin added, it is desirable to adjust the amount of phloroglucin added twice the theoretical. Therefore, expe iments were made on the mixtures of glucose and xylose (3 g. of glucose 10, 30, 50 and 100 mg. of xylose) adding twice plus the theoretical amount of phloroglucin to the distillate.

Results in Table 6 indicate the alcohol-extraction is useful especially for pentosan-poor samples,

Table 6

Solubility of Phloroglucide from Glucose-Xylose Mixtures

Sample, glucose 3 g. plus xylose, mg.	Xyolse, observed, mg.	
	without alc.	with alc.
10	72.6	17.0
30	90.5	36.1
50	105.5	58.7
100	151.8	112.0

but even in those cases, the amount of xylose observed is always greater than the true value. This is due to the presence of a greater amount of alcohol-insoluble phloroglucide from oxymethyl furfural than an alchool-soluble part of furfural-phloroglucide.

(d) **Discussion.**—The amount of alcohol-soluble phloroglucide of furfural increased with the amount of phloroglucin added. This indicates that the structure of furfural-phloroglucide is not constant. But, as above mentioned, the total amount of phloroglucide is independent of the phloroglucin added and consistent with the assumption that one mole of furfural condenses with one mole of phloroglucin under dehydration of two moles of water. From these results, the condensate is thought to be a relatively high-molecular compound as in furfural resin, with structures of chain type or more probably net-work type, and not to be a low-molecular compound. The size and shape of the condensate would vary with phloroglucin added and influence the solubility in alcohol. A distinct conclusion, however, can not be made without elementary analysis and molecular weight determination of the condensate.

In the case of oxymethyl furfural, the added amount of phloroglucin dose not influence the solubility in alcohol but the color change above mentioned may show structural variation of the condensate similar to the case of furfural-phloroglucide. In both cases, if the precipitate was

once dried, the solubility in alcohol was lowered perhaps by increased condensation. Even when wet, undried precipitate was treated with alcohol, and the solubility was considerably influenced by the method of filtration and the duration of time from filtration to the alcohol-treatment.

In conclusion, the alcohol-treatment of phloroglucide is useful to reduce remarkably the influence of hexosan on pentosan determination, but has the defects that the influence is not completely removed and the experimental reproducibility is not good because of complicated factors.

III. Colorimetry with Aniline and Comparison with Other Methods

1) Experimental Procedures.—Pentosan determination by colorimetry was in most cases applied to furfural produced by acid-distillation, but sometimes also applied to pentose itself obtained by acid hydrolysis.[17] Many color reagents such as benzidine,[18] xylidine,[19] orcin,[20] aniline[6]~[9] and p-bromoaniline[21] were used. It soon became evident from the preliminary work that the method of Stillings & Browning[8] gave good results. Then, this method was adopted with the following modifications.

Acetic acid-aniline reagent was prepared by dissolving 50 cc. of aniline in 500 cc. of glacial acetic acid. To 10 cc. of the neutralized distillate 50 cc. of the aniline solution was added and kept standing for half an hour at 25°C. Transmittancy of the solution was determined by the Hitachi EPO type photometer with a filter of 520 mμ, and compared with standard solution of furfural. In this and following experiments distillation was continued to 270 cc. to save the time of distillation. Furthermore, too long distillation gave rise to much quantity of oxymethyl furfural produced by side reaction (cf. Fig. 1).

2) Experimental Results.—Stability of the color reaction with aniline depends on temperature. As temperature lowers, rate of decolorization decreases and the stability increases as shown in Fig. 2. Colorimetry with aniline was applied to glucose-xylose mixtures and the results were compared with other methods as shown in Table 7. In Table 8, pentosan content in some cellulosi

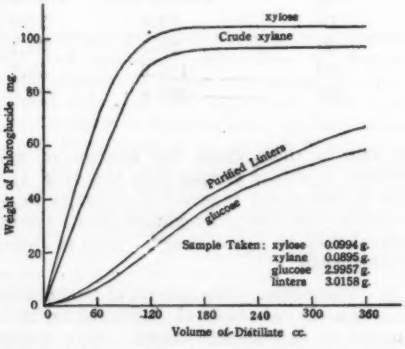

Fig. 1.—Effect of volume of distillate on the amount of phloroglucide produced.

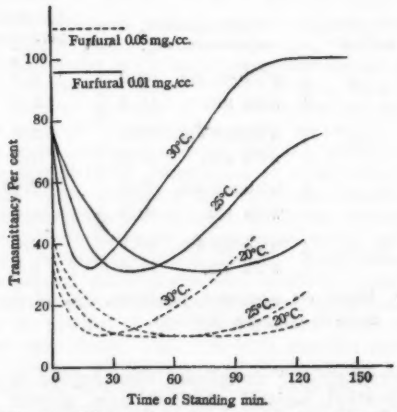

Fig. 2.—Effect of temperature on transmittancy.

Table 7

Comparison of Various Methods for Pentosan Determination

Sample, g.		Xylose, % theoretical	Xylose, % observed				
Glucose	Xylose		Barbituric acid	Bromate	Phloroglucin		Colorimetry
					without alc.	with alc.	
3.00	0	0	0	2.1	2.0	0.5	0.1
3.00	0.01	0.33	0	2.2	2.4	0.6	0.3
3.00	0.03	0.99	0	3.1	3.0	1.2	1.0
3.00	0.05	1.63	0	3.6	3.5	1.9	1.5
3.00	0.10	3.23	2.5	4.9	4.9	3.6	3.3

(17) G. L. Miller, R. H. Golder and E. E. Miller, *Anal. Chem.*, **23**, 903 (1951).
(18) R. A. McCance, *Biochem. J.*, **20**, 1111 (1926).
(19) K. Sumikura and Z. Nakamura, *Labr. Biol. Tokori Coll.*, 158 (1928).
(20) Analysis Comittee of the Central Laboratory of the Cellulose Industry, *Svensk Papperstid.*, **54**, 179 (1951).
(21) E. W. Rice, *Anal. Chem.*, **23**, 1501 (1951).

materials was determined by colorimetry. It was assumed that, in Table 8, pentosan in the samples was only xylan[22] and in Tables 6~8, conversion ratio of xylose to furfural was 86%.

Table 8

Pentosan Content in Some Cellulosic Materials (Colorimetrically Determined)

Sample	Pentosan, %
Unbleached pulp for viscose rayon	2.46
Purified pulp for cellulose ester	0.61
Rayaceta	0.74
Secondary cellulose acetate from Rayaceta	0.25
Secondary cellulose acetate (Hercules)	0.37
Secondary cellulose acetate (Eastman)	0.36
Viscose staple	0.92
Viscose rayon	0.53
Bleached linters	0.25
Raw Egypt cotton (alcohol-benzene extracted)	0.50

3) **Discussion.**— Table 7 shows that, for the estimation of a small quantity of pentosan, the colorimetry is superior to other methods. The next one is phloroglucin method with the alcohol-treatment. But, as already mentioned before, experimental reproducibility of the latter is inferior to that of the colorimetry and the method gives high values to pentosan-poor materials and presumably low values for pentosan-rich ones, because of partial solubility of furfural and oxymethyl furfural-phloroglucide in alcohol. Barbituric acid method[1] gives always low values and especially for the samples, in which pentosan content is under 1.5%, no precipitate being formed. Bromate method[23] (not corrected for oxymethyl furfural) agrees very well with phloroglucin method[24] without the alcohol-treatment but they give a higher result (about 2%) than the true value. This higher value (2%) might seem too large as compared with the values reported by other investigators but it may be accounted for by the differences in distillation apparatus and conditions which affect the amount of oxymethyl furfural as mentioned before, or for the characteristics of cellulose materials as pointed out by Meller.[25]

In conclusion, colorimetry is superior to other methods for the determination of a small quantity of pentosan. Phloroglucin method with alcohol-treatment considerably removes the influence of hexosan and has a limited usefulness.

(22) H. Sobue and A. Hateno, *J. Chem. Soc. Japan, Ind. Chem. Sec.*, **55**, 131 (1952).
(23) *Tappi Standard* T 19 m-50 (1950).
(24) *Tappi Standard* T 223 m-48 (1943).
(25) A. Meller, *Paper Trade J.*, **124**, No. 9, 104 (1947); **125**, No. 11, 57 (1947).

Summary

1. For the estimation of a small quantity of pentosan in cellulosic materials, an improvement of phloroglucin method and colorimetry with aniline were investigated on mixtures of glucose and xylose, and the results were compared with bromate, the usual phloroglucin and barbituric acid methods.

2. Treatment of the undried phloroglucide with alcohol remarkably removes the influence of hexosan on pentosan determination but it is not complete. As the solubility of the furfural-phloroglucide increases with phloroglucin added, it is desirable to increase the amount of the latter to twice the theoretical.

3. Colorimetry with aniline is superior to other methods. The color reaction is stable at low temperatures.

4. Pentosan contents of some cellulosic materials, such as rayons, pulps and cellulose acetates, are tabulated.

We express thanks to Masao Moriya for his earnest aid throughout the experiment. The expense of this work was defrayed from the Scientific Research Encouragement Grant of the Department of Education.

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The Normal Vibrations of Some Silicon Tetrahalides as Calculated by Urey-Bradley Field

By Yuzo KAKIUTI

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Assuming the Urey-Bradley field, Simanouti calculated the normal frequencies of many polyatomic molecules which are in good agreement with the observed values.[1][2][3] In the present paper, the normal frequencies of some silicon tetrahalides were calculated using the similar type of potential field, according to which the potential energy of a molecule can be expressed as follows,

$$V=\sum_i\left[K'_i r_i \Delta r_i+\frac{1}{2}K_i(\Delta r_i)^2\right]$$
$$+\sum_{i<j}\left[H'_{ij} r^2_{ij}\Delta\alpha_{ij}+\frac{1}{2}H_{ij}(r_{ij}\Delta\alpha_{ij})^2\right]$$
$$+\sum_{i<j}\left[F'_{ij}q_{ij}\Delta q_{ij}+\frac{1}{2}F_{ij}(\Delta q_{ij})^2\right],$$

where the notations same as those given in reference (1) are used. K, H and F denote stretching, bending and repulsive force constants, respectively. The values of these force constants were determined so as to give the best fit with the observed frequencies of $SiCl_4$, $SiBr_4$ and SiI_4, taking the equilibrium bond distances Si-Cl, Si-Br and Si-I as 2.01, 2.15 and 2.43 A, respectively (see Table 1). Here

Table 1

Values of the force constants (K, H, F, $F'\times10^{-5}$ dyne/cm and $\kappa\times10^{11}$ dyne.cm)

$SiCl_4$		$SiBr_4$		SiI_4	
K (Cl) =	2.59	K (Br) =	2.02	K (I) =	1.48
H (Cl) =	0.059	H (Br) =	0.051	H (I) =	0.044
F (Cl) =	0.29	F (Br) =	0.23	F (I) =	0.16
F' (Cl) =	−0.029	F' (Br) =	−0.023	F' (I) =	−0.016
κ (Cl) =	0.21	κ (Br) =	0.18	κ (I) =	0.14

The κ's denote the intramolecular tensions.

we assumed that F' value is about −10 % of F value.[4] Some of these values agree very well with those given in reference (3). Using

Table 2

Calculated *vs.* observed frequencies (cm^{-1})

Class		Obs.[5]	Calc.	Diff. %
$SiCl_4$	A_1	424	424	0
	E	150	150	0
	F_2	221	220	−0.5
		610	608	−0.3
$SiBr_4$	A_1	249	250	+0.4
	E	90	91	+1.1
	F_2	137	138	+0.7
		487	488	+0.2
SiI_4	A_1	168	168	0
	E	63	63	0
	F_2	94	94	0
		405	405	0
$SiClBr_3$	A_1	159	159	0
		288	291	+1.0
		579	584	+0.9
	E	101	102	+1.0
		173	162	−6.4
		498	491	−1.4
$SiCl_2Br_2$	A_1	111	111	0
		182	181	−0.5
		326	329	+0.9
		563	565	+0.4
	B_1	191 (?)	187	−2.1
		605	604	−0.2
	B_2	174	174	0
		508	494	−2.8
	A_2	122	123	+0.8
$SiCl_3Br$	A_1	191	187	−2.1
		368	370	+0.5
		545	540	−0.9
	E	135	134	−0.7
		205	206	+0.5
		610	606	−0.7
$SiCl_2I_2$	A_1	114	117	+2.6
		220	228	+3.6
		557	570	+2.3
	E	73	74	+1.4
		134	138	+3.0
		411	436	+6.1

(1) T. Simanouti, *J. Chem. Phys.*, **17**, 245 (1949).
(2) T. Simanouti, *ibid.*, **17**, 734 (1949).
(3) T. Simanouti, *ibid.*, **17**, 848 (1949).
(4) T. Simanouti, to be published shortly.
(5) M. L. Delwaulle, *J. Phys. Chem.*, **56**, 355 (1952).

Class	Obs.[5]		Calc.	Diff. %
$SiCl_2I_2$	A_1	83	83	0
		160	161	+0.6
		276	281	+1.8
		538	544	+1.1
	B_1	?	165	
		589	599	+1.7
	B_2	149	150	+0.7
		418 / 436	421	
	A_2	111	114	+2.7
$SiCl_3I$	A_1	169	165	−2.4
		333	333	0
		519	511	−1.5
	E	123	125	+1.6
		197	199	+1.0
		600	603	+0.5

the common values of these force constants, the normal frequencies of $SiCl_4$, $SiBr_4$, SiI_4, $SiCl_3Br$, $SiCl_2Br_2$, $SiClBr_3$, $SiCl_3I$, $SiCl_2I_2$ and $SiClI_3$ were calculated in the same way as in reference (1), where we assumed that the force constants relating to both unlike halogen atoms X and Y have the average values of two force constants which are concerned with each of them. The results are shown in Table 2. The calculated frequencies are in general in good agreement with the observed values.

The writer wishes to express his sincere thanks to Prof. S. Mizushima at Tokyo Univ. and Dr. T. Simanouti for their kind guidance.

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Antituberculous Compounds. III. N-Acyl Derivatives of *p*-Aminocinnamaldehyde and *p*-Aminobenzaldehyde thiosemicarbazones[1]

By Tamio NISHIMURA

(Received November 29, 1952)

Several N-acyl derivatives of *p*-aminocinnamaldehyde thiosemicarbazone were prepared in order to study the effects of a variety of acyl groups on its antituberculous activity. In the course of this study, it was found that *p*-dimethylacrylylaminocinnamaldehyde thiosemicarbazone, when tested by subcutaneous injection of its oily suspension,[2] had markedly reduced toxicity compared with other thiosemicarbazones prepared in this laboratory. As it was considered that this effect would be due to the presence of α,β-double bond in dimethylacrylyl radical, the experiment was extended to combine α,β-unsaturated acids having fewer carbon atoms with *p*-aminocinnamaldehyde and *p*-aminobenzaldehyde thiosemicarbazones. The preparation of the higher analogs was not undertaken since the higher acyl groupings seemed to decrease the activity.[3]

Dimethylacrylic acid was prepared by the usual method.[4][5][6] Dimethylacrylyl chloride was first prepared by the action of thionyl chloride on dimethylacrylic acid[7] in unsatisfactory yields, but later phosphorus trichloride was found to give a better yield and pure material. Phenylacetyl chloride and cinnamyl chloride were employed in the experiments, in the form of etheral solutions without isolation of the substances.[8] Methacrylic acid was prepared by hydrolysis of methyl methacrylate[9] and the corresponding chloride was obtained according to the method described by Rehberg et al.[10] *p*-Aminocinna-

(1) Most part of this study has been presented before the annual meeting of the Chemical Society of Japan in Tokyo on April 5, 1952.

(2) Toraichi Takebe, Unpublished data.

(3) Katsuhiko Tago, Unpublished data; Robert Behnish, Fritz Mietsch and Hans Schmidt, *Am. Rev. of Tuberc.*, **61**, 1 (1950).

(4) J. B. Conant and Neal Tuttle, *Org. Syn.* Col, Vol. 1, p. 193.

(5) J. B. Conant and Neal Tuttle, Ibid., p. 338.

(6) Barbier and Léser, *Bl.* (3) 33, 815.

(7) H. Staudinger and E. Ott. *Ber.*, **44**, 1636 (1911).

(8) G. A. Schmidt and David A. Shirley, *J. Am. Chem. Soc.* **71**, 3804 (1948).

(9) Ryozo Inoue, *J. Soc. Chem. Ind., Japan*, **45**, 385 (1942).

(10) C. E. Rehberg, Marion B. Dixon and C. H. Fisher, *J. Am. Chem. Soc.* **67**, 208 (1945).

Table 1

Thiosemicarbazones

Aldehydes	Yield %	Solvent for recrystallization	M. P. °C	Empirical formula	Nitrogen % Calcd.	Nitrogen % Found
p-Benzoylamino-cinnamaldehyde[a]	43	pyridine and water	233—4 (decomp.)	$C_{17}H_{16}ON_4S$	17.23	17.37
p-Phenylacetylamino-cinnamaldehyde[b]	39	pyridine and water	223 (decomp.)	$C_{18}H_{18}ON_4S$	16.56	16.65
p-Dimethylacrylyl-aminocinnamaldehyde[a]	53	pyridine and water	234—5 (decomp.)	$C_{15}H_{18}ON_4S$	18.55	18.27
p-Dimethylacrylyl-aminobenzaldehyde[a]	39	glacial acetic acid	224 (decomp.)	$C_{12}H_{16}ON_4S$	20.27	20.17
p-(*p*-Tolylsulfonyl)-aminocinnamaldehyde[a]	73	pyridine and water	241—2 (decomp.)	$C_{17}H_{18}O_2N_4S_2$	14.94	15.06
p-*n*-Caproylamino-cinnamaldehyde[a]	46	ethanol	197	$C_{16}H_{22}ON_4S$	17.60	17.44
p-*n*-Caproylamino-benzaldehyde[a]	53	ethanol	201 (decomp.)	$C_{14}H_{20}ON_4S$	19.16	18.84

(a) Pure chloride was used. The reaction was carried out in pyridine.

(b) This substance was prepared as with *p*-cinnamylaminocinnamaldehyde thiosemicarbazone.

maldehyde and *p*-aminobenzaldehyde thiosemicarbazones could be prepared smoothly by the reduction of the corresponding nitrothiosemicarbazones with sodium hydrogen sulfide.[11]

All the N-acyl derivatives of *p*-aminocinnamaldehyde and *p*-aminobenzaldehyde thiosemicarbazones except for succinoyl and crotonyl derivatives were obtained by the action of acid chloride or its etheral solution on the amino thiosemicarbazones in pyridine. An attempted preparation of the crotonyl derivatives in pyridine did not succeed, but Schotten-Baumann's reaction in methyl acetate gave the desired products in reasonable yields. The compounds not described in the experimental part are listed in Table 1.

Biological evaluations of these thiosemicarbazones will be published elswhere. This paper is concerned only with their synthesis and characterization.

Experimental[12]

β, β-Dimethylacrylyl Chloride.—A mixture of 10 g. of dimethylacrylic acid and 7.5 g. of phosphorus trichloride was warmed at 60—75° for 3.5 hours. The crude chloride obtained by distillation under reduced pressure was further subjected to distillation under ordinary pressure and a portion boiling at 145—150° and amounting to 7.7 g. (65%) was collected.

***p*-Aminobenzaldehyde Thiosemicarbazone.**—200 cc. of ethanol and 80 cc. of 2 N-sodium hydroxide solution were mixed, saturated with hydrogen sulfide and 22.4 g. of *p*-nitrobenzaldehyde thiosemicarbazone was added in one portion. The whole mixture was then refluxed on a steam bath for 30 minutes, while the crystals of the nitro thiosemicarbazone completely disappeared. A resulting dark red colored solution was allowed to stand at room temperature overnight and the separated crystals were collected on a filter, and were washed thoroughly with ethanol and water. Dried material, m. p. 197—198° (decomp.) weighed 14.5 g. (75%).

***p*-Succinoylaminocinnamaldehyde Thiosemicarbazone.**—A mixture of 2.2 g. of *p*-aminocinnamaldehyde thiosemicarbazone, 1.0 g. of succinic anhydride and 20 cc. of ethylacetate was refluxed for 30 minutes. The precipitate was collected, dissolved in sodium hydroxide solution, and the filtered solution was acidified with 10% hydrochloric acid to give 2.2 g. (70%) of the desired product melting at 189° (decomp.). A small sample was recrystallized from ethanol to yield a pure product, m. p. 207—208° (decomp.) (Found: N, 17.47%. Calcd. for $C_{14}H_{16}O_3N_4S$; N, 17.50%).

***p*-Crotonylaminobenzaldehyde Thiosemicarbazone.**[13]—To a mixture of 3.9 g. of *p*-aminobenzaldehyde thiosemicarbazone, 10 cc. of 2N-sopium hydroxide solution and 60 cc. of methylacetate were added dropwise. And then a solution of 2.1 g. of crotonyl chloride in 10 cc. of methylacetate at 5—10° was added with stirring. Yellow crystals were collected, washed with methylacetate and dried, yielding 2.4 g. (46%) of the desired product melting at about 240° (decomp.). On dissolving it in 56 cc. of pyridine and adding 110 cc. of water to the solution, long needles (2.0 g.) of the same m. p. separated. For microanalysis a portion was further recrystallized from ethanol (Found: N, 21.04. Calcd. for $C_{12}H_{14}ON_4S$: N, 21.36%).

(11) Tamio Nishimura, This Bulletin, **25**, 54 (1952).

(12) All temperatures are uncorrected.

(13) Crotonyl chloride was prepared by the action of phosphorus trichloride on α-crotonic acid.

***p*-Crotonylaminocinnamaldehyde Thiosemicarbazone.**[13]—From 2.2 g. of *p*-aminocinnamaldehyde thiosemicarbazone, 2.4 g. (83%) of the acylated product melting at 222° (decomp.) was obtained in a manner similar to that described above. It was dissolved in 16 cc. of pyridine and 30 cc. of water was added to the solution. Yellow crystals (1.1 g.) of m. p. 227° (decomp.) were collected, redissolved in 20 cc. of pyridine and 40 cc. of water was added to the solution, giving 1 g. (35%) of the pure material melting at 234° (decomp.). An additional recrystallization was without effect on the m. p. (Found: N, 19.40%. Calcd. for $C_{14}H_{16}ON_4S$: N, 19.43%).

***p*-Cinnamoylaminocinnamaldehyde Thiosemicarbazone.**—A mixture of 0.74 g. of cinnamic acid and 0.60 g. of thionyl chloride was heated at 70—90° for an hour and the unreacted thionyl chloride removed by distillation. The residual acid chloride dissolved in ether was added dropwise and with stirring to a cold solution of 1.1 g. of *p*-aminocinnamaldehyde-thiosemicarbazone in pyridine and the reaction mixture was poured into 150 cc. of ice water. The solid was recrystallized by means of pyridine and water; yield 0.6 g. (33%) m. p. 243° (decomp.) (Found: N. 15.60%. Calcd. for $C_{19}H_{18}ON_4S$: N, 15.96%).

***p*-Methacrylylaminobenzaldehyde Thiosemicarbazone.**—A mixture of 1.3 g. of methacrylic acid and 0.7 g. of phosphorous trichloride was kept at 60—70° for fifteen minutes and then at room temperature for two hours. The upper layer was added dropwise to a cold solution of 2 g. of *p*-aminobenzaldehyde thiosemicarbazone in 10cc. of pyridine. After standing at room temperature for an hour, 15 cc. of water was added to the reaction mixture and allowed to stand in an ice box over-night. The separated solid, after recrystallizations from pyridine and water, gave 0.4g. of colorless plate melting at about 216° (decomp.) (Found: N, 20.93%, Calcd. for $C_{12}H_{14}ON_4S$: N, 21.36%).

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Dephosphorylation of Nucleic Acids, Mononucleotides and Casein by Lanthanum and Cerium Hydroxide Gels

By Michio SHIMOMURA and Fujio EGAMI

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E. Bamann[1] has found that certain metal hydroxide gels, especially those of lanthanum and cerium, have catalytic effect on the hydrolysis of phosphate esters. Since nucleic acids are also phosphate esters, we studied the behavior of yeast ribonucleic acid towards lanthanum hydroxide gel and have found that it is easily dephosphorylated.[2] Independently of us, and probably of Bamann, K. Dimroth and his coworkers quite recently reported the similar effects of metal hydroxide gels.[3] J. E. Backer and F. W. Allen,[4] on the other hand, showed that pyrimidine nucleotides could be hydrolysed into nucleosides and inorganic phosphate under similar conditions.

The present paper deals with our recent studies on the catalytic effects of lanthanum and cerium hydroxide gels.

Materials

Two preparations, free acid and sodium salt, of brewer's yeast RNA, designated as RNA Preparation 1 and 2, were used. These were extracted by the method of Clarke and Schryver.[5] In obtaining Preparation 2, the chloroform method of Sevag et al.[6] was used. The phosphorus content of the two preparations was 6.5 and 8.7 per cent, respectively. The highly polymerized preparation of the sodium salt of calf spleen DNA, containing 7.4 per cent phosphorus, was

(1) E. Bamann, *Angew. Chem.*, **52**, 186 (1939).
(2) F. Egami and M. Shimomura, *Science (Japan)*, **18**, 472 (1948).
(3) K. Dimroth, L. Jaenicke and D. Heinzel, *Ann. Chem.*, **566**, 206 (1950). K. Dimroth, L. Jaenicke and I. Vollbrechtshausen, *Z. physiol. Chem.*, **289**, 71 (1952).
(4) J. E. Backer and F. W. Allen, *J. Biol. Chem.*, **188**, 59 (1951).
(5) G. Clarke and S. B. Schryver, *Biochem. J.*, **11**, 319 (1937).
(6) M. G. Sevag, D. B. Lackman and J. Smolens, *J. Biol. Chem.*, **124**, 425 (1938).

kindly supplied by Dr. A. Sibatani. Desoxyribo-, a-ribo-, b-ribo and 5'-ribocytidylic acid were kindly supplied by Dr. W. E. Cohn. The phosphorus content of commercial casein prepared by the method of Hammersten was 0.80 per cent.

Lanthanum carbonate was prepared from industrial lanthanum oxide. Since the latter contained silicates and metaphosphates, which hinder the action of lanthanum hydroxide and disturb the estimation of phosphoric acid detached from substrates, these impurities were removed during the course of preparation of the carbonate by heating with hydrochloric acid and then with sodium hydroxide and finally by treating the mixture with ammonium molybdate. Cerium carbonate was likewise prepared from industrial cerium oxide.

Experimental Conditions

The reaction mixture in a typical experiment for the measurement of dephosphorylation of RNA: 100 mg. of lanthanum carbonate were suspended in distilled water and dissolved by the addition of hydrochloric acid in a 50 cc. Erlenmeyer flask. Then it was adjusted to *p*H 8.0 by aqueous ammonia, thus lanthanum hydroxide was precipitated. To this suspension, 1 cc. of 1 per cent RNA solution, 10 cc. of 0.1 N sodium veronal-hydrochloric acid buffer, *p*H 8.0, and water were added till the final volume was 20 cc. RNA formed additional precipitate with lanthanum ion, known as a powerful precipitating reagent for nucleic acids.[7] The flask was rubber-stoppered, shaken vigorously to make the suspension homogeneous and immersed in a water-bath, which was held at desired temperature (time zero.). The mixture was shaken occasionally during the hydrolysis to avoid precipitation. Aliquots of 1 to 2 cc. were withdrawn at various time intervals, cooled to room temperature if necessary, and analysed for inorganic phosphate. Similar conditions were also used when the dephosphorylation of phosphoric esters other than RNA were tested.

Analytical Methods

Total Phosphorus.—The phosporus content of the various preparations was measured by the method of Lieb and Wintersteiner.[8]

Inorganic Phosphate.—In the reaction mixtures, phosphate was found only in the precipitate and was completely absent in the supernatant. Samples for analysis, therefore, were withdrawn carefully avoiding uneven sampling.

In reaction mixtures containing nucleic acid or protein, the bulk of these substances was precipitated by the addition of an equal volume of 10 per cent trichloroacetic acid. This technique permitted the direct colorimetric determination of the phosphate in the supernatant according to the method of Fiske and Subbarow.[9] The decrease of the colour intensity due to the presence of lanthanum was negligible within concentrations used. A slight turbidity which appeared on addition of the molybdate was removed by centrifugation.

Reducing Power.—If the glycosidic linkage in nucleosides is broken during the hydrolysis of RNA, the appearance of a reducing group is to be expected. This was measured by the ferricyanate reduction method of Fujita and Iwatake,[10] in which the lanthanum contained in the test samples was removed together with cadmium hydroxide.

Orcinol Reaction for the Estimation of RNA and Diphenylamine Reaction for the Estimation of DNA—Methods described by Kerr and Seraidarian[11] and by Dische[12] were used respectively; the presence of lanthanum did not disturb the estimations.

Experimental

Effect of Temperature.—Fig. 1 shows the dephosphorylation reaction of RNA by lanthanum hydroxide gel at various temperatures. It was observed that 95 per cent of the total phosphate groups of RNA were transformed into inorganic phosphate in 24 hours both at 90° and at 100°. In a control experiment at 80°, in which lan-

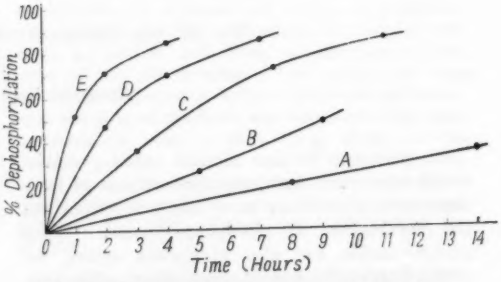

Fig. 1.—Effect of temperature on the hydrolysis of ribonucleic acid under the influence of lanthanum hydroxide. Each reaction mixture contained 10 mg. of RNA Preparation 2, lanthanum hydroxide (from 100 mg. of lanthanum carbonate), and 10 cc. of 0.1 N veronal buffer, *p*H 8.0, the total volume 20 cc. Curves A, B, C, D and E are at 60°, 70°, 80°, 90° and 100°, respectively. Curves D and E reached at 95 per cent dephosphorylation in 24 hours.

(7) E. Hammersten and T. Theorell, *Acta Med. Scand.*, **68**, 226 (1928).
(8) H. Lieb and O. Wintersteiner, *Mikrochemie*, **2**, 78 (1924).
(9) C. H. Fiske and Subbarow, *J. Biol. Chem.*, **66**, 375 (1925).
(10) A. Fujita and D. Iwatake, *Biochem. Z.*, **242**, 43 (1932).
(11) S. E. Kerr and K. Seraidarian, *J. Biol. Chem.*, **159**, 211 (1945).
(12) Z. Dische, *Mikrochemie*, **2**, 26 (1930).

thanum was omitted, no formation of inorganic phosphate was observed. On the other hand, the dephosphorylation of RNA was very slow at low temperatures. The amount of inorganic phosphate was only 2 per cent at 28° and 0 per cent at 5° after 5 days.[13]

The activation energy of the dephosphorylation reaction of RNA under the influence of lanthanum hydroxide was calculated from Fig. 1. The reaction was approximately of the first order, at least before 80 per cent dephosphorylation. Log k and $1/T$ were in linear relation between 60° and 100°. The activation energy was 20,200~20,400 cal.

Effect of *p*H.—The influence of *p*H on the lanthanum hydroxide is illustrated in Fig. 2. Optimal *p*H lies between 8.0 and 9.0.

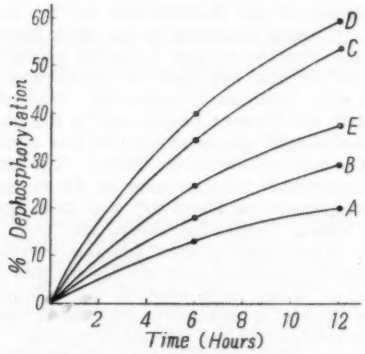

Fig. 2.—Effect of *p*H on the hydrolysis of ribonucleic acid under the influence of lanthanum hydroxide. Curves *A*, *B*, *C*, *D* and *E* are at *p*H 6.0 (citrate buffer), 7.0 and 8.0 (veronal buffer), 9.0 and 10.0 (ammonium buffer), respectively. Temperature 70°. Other conditions similar to Fig. 1.

Effect of the Quantity of Lanthanum hydroxide.—The catalytic effect of lanthanum hydroxide increased with increasing quantity (Fig. 3). The atomic ratio of lanthanum/phosphorus in the reaction mixture in which 10 mg. of lanthanum carbonate was used was approximately 1 (Curve *B*). After 40 hours Curves *B*, *C* and *D* reached 100 per cent, whereas Curve A barely reached 70 per cent. This was understandable since the phosphate formed during the hydrolysis of RNA hindered the catalytic effect by firmly attaching itself to lanthanum.

Natures of the Hydrolysis Product—RNA was almost completely dephosphorylated under the relatively mild conditions, and the nucleosides, the dephosphorylation product, were expected to remain unaltered under these conditions. The

(13) The data at low temperatures reported in the previous paper (2) had been slightly higher, since the inorganic phosphate had been estimated by the method of Bell and Doisy, and hence the colour due to silicates had been contaminated.

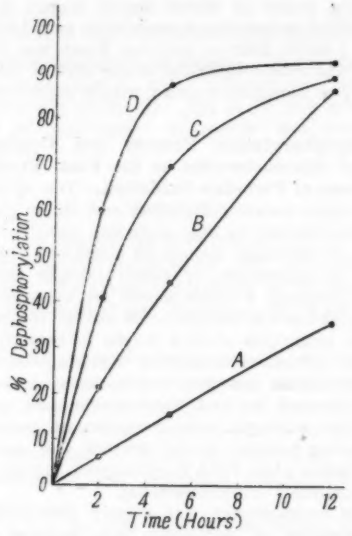

Fig. 3.—Effect of the amount of lanthanum hydroxide on the hydrolysis of ribonucleic acid. Curves *A*, *B*, *C* and *D* were obtained with lanthanum hydroxide produced respectively from 5, 10, 30 and 100 mg. of lanthanum carbonate. Temperature 90°. Other conditions similar to Fig. 1.

Table 1

Reducing Power and Colour Intensity of Orcinol Test during Dephosphorylation of RNA

Time, hrs	Dephosphorylation, %	Reducing Power† mg. glucose	Orcinol Test†† %
0		0.00	103
1		0.00	100
12		0.00	100
25		0.00	100
39		0.00	97
43	98	0.01	97
Calculation		1.25*	

The reaction mixture contained 50 mg. of RNA Preparation 2, lanthanum hydroxide obtained from 500 mg. of the carbonate, and 25 cc. of 0.1 M veronal buffer, *p*H 8.0, in a total volume of 50 cc. Temperature, 80°. 3 cc. of reaction mixture was used for each estimation of reducing power.

† Reducing power measured with 3 cc. aliquots and expressed as mg. glucose.

†† The colour intensities measured were compared with the standard RNA solution containing RNA in the same concentration as the original reaction mixture.

* On the complete hydrolysis of the glycosidic linkages.

reducing power of ribose should appear, if the glycosidic linkages in the nucleosides were broken; Table 1 shows that no reducing group was liberated. The colour intensity of the orcinol test for ribose also remained constant within experimental error.

Dephosphorylation Process and Confirmation of Ribonucleosides as the Final Products by Means of Periodate Oxidation.—The splitting of linkages between the bases and ribose groups may be detected by the periodate test.[14] One mole of periodate should be consumed per one mole of nucleosides, if these linkages remain intact, whereas, 4 moles should be consumed, if the breakdown is complete. Moreover, the course of the hydrolysis of RNA might be investigated by this periodate oxidation method, since 5′-ribonucleotides consume one mole of periodate per mole, but 2′- and 3′-ribonucleotides would not. For example, the formation of periodate consuming products would precede the dephosphorylation when RNA is hydrolysed through the intermediate 5′-ribonucleotides.

Since measurement was greatly disturbed by the existence of lanthanum salt, samples were mixed with an equal volume of 0.2 M phosphate buffer, *p*H 7.0, thus inducing the complete precipitation of lanthanum in the form of insoluble phosphate. After standing for about 10 minutes and centrifugation, aliquot of these supernatants was used for the periodate test. Another aliquot of these supernatants was examined by the orcinol test for ribose. The result of this test showed that the amount of RNA removed together with lanthanum was relatively small (Column 3, Table 2). Table 2 shows that the consumption of periodate precedes the dephosphorylation. It may be explained by the fact shown below (see Table 3) that the phosphate at 2′- or 3′-carbon atom is split off preferentially in comparison to that at 5′-carbon atoms. The fact that the final product consumes approximately one mole of periodate per mole of total phosphorus confirms the already mentioned finding that nucleosides are the final hydrolysis product.

Preparation of Ribonucleosides.—60g. of lanthanum carbonate were suspended in distilled water and dissolved by the addition of distilled hydrochloric acid. After precipitating lanthanum hydroxide from the solution by the addition of concentrated aqueous ammonia, the precipitate was washed thoroughly with dilute aqueous ammonia by centrifugation in order to remove the chlorine ion. The precipitate was finally suspended in distilled water. To this lanthanum hydroxide suspension was added RNA solution containing 20 g. of RNA Preparation 1. This mixture was adjusted at *p*H 8 to 9 with aqueous ammonia or with sulphuric acid. Total volume was about 1.5 liter. The mixture was heated to 80° and maintained at this temperature for about 40 hours. Aqueous ammonia was added occasionally to prevent lowering of *p*H. Then, the precipitate was filtered off and washed with 1.5 liter of hot water. (Protein, contained in the RNA Preparation, was adsorbed to, and inorganic phosphate, produced by the hydrolysis of RNA, was also bound with lanthanum hydroxide. Nucleosides went into the filtrate.) Lanthanum in the filtrate was precipitated quantitatively by the addition of oxalic acid and filtered by suction. The filtrate was concentrated to a volume of 300 cc. under reduced pressure at about 50° and then filtered while warm. Guanosine settled out from the filtrate in long needles upon freezing overnight. This was recrystallized from hot water. The yield was 2.1 g. Picric acid solution was then added to the filtrate of guanosine until there was no further precipitation of adenosine picrate. The picrate was filtered off and a second crop was obtained when the filtrate was concentrated to 400 cc. and allowed to stand in a refrigerator. The picrate was crystallized from hot water in the form of platelets. The yield was 4.0 g. Finally cytidine picrate was obtained in the form of long crystalline needles from the filtrate of adenosine picrate by the method of Levene.[15] The yield was 3.2 g.

Behaviour of Desoxyribonucleic Acid.—No dephosphorylaton of DNA was observed under

Table 2

Periodate Consumption by Hydrolysis Product in the Course of Dephosphorylation of RNA

Time, hrs	Dephosphorylation, %	Colour intensity of orcinol test, %	Periodate, consumption mole	Periodate consumption Colour intensity of orcinol test, mole
0	0	73	0.025	0.034
2	25	78	0.59	0.76
5	54	96	0.84	0.87
8	72	96	1.06	1.10
23	99	104	1.22	1.17

The reaction mixture contained 100 g. of RNA Preparation 2 and lanthanum hydroxide obtained from 300 g. of the carbonate. Total volume, 20 cc.; *p*H, 8.0; temperature, 80°. No buffer was used and occasional addition of N sodium hydroxide prevented the lowering of *p*H.

(14) R. Adams, "Organic Reaction," New York, **2**, 341 (1944).

(15) P. A. Levene, *J. Biol. Chem.*, **25**, 103 (1916).

the same conditions as shown in Curve 3 in Fig. 1 even after 48 hours. The supernatant of the reaction mixture at 48 hours gave negative diphenylamine test, although, in the case of RNA, the colour intensity of the orcinol test of the supernatant increased with increasing dephosphorylation of RNA. DNA, even after the depolymerization by heating in 0.25 N sodium hydroxide at 80° for 20 minutes, was not dephosphorylated under the influence of lanthanum hydroxide.

Dephosphorylation of Nucleotides.—Contrary to DNA, desoxyribocytidylic acid was dephosphorylated. Table 3 shows the dephosphorylation of desoxyribo- and ribonucleotides. b-Cytidylic acid is dephosphorylated more easily than a-cytidylic acid and 5′-cytidylic acid most slowly.

Table 3

Dephosphorylation of Various Cytidylic Acids

Time, hrs.	Desoxyribo-, %	a-Ribo-, %	b-Ribo-, %	5′-Ribo-, %
3	60	57	89	30
6	88	85	97	43
Control				
12	0	3.0		

The reaction mixture contained lanthanum hydroxide obtained from 30 mg. of the carbonate, nucleotide (1.92 mg. desoxyribo-; 2.08 mg. a-ribo-; 2.31mg. b-ribo-; 2.05mg. 5′-ribocytidylic acid, in each case), and 1 cc. of M ammonium buffer, *p*H 9, and the volume was made to 12 cc. with distilled water.

Table 4

Catalytic Effect of Lanthanum Hydroxide on Dephosphorylation of Casein

Time, hrs	Dephosphorylation at 25°, %	Dephosphorylation at 70°, %	Control, at 70°, %
18.5		71	20
21.5	0		
42.5		98	34

Each reaction mixture contained 50 mg. of casein, lanthanum hydroxide obtained from 150 mg. of the carbonate, 1 cc. of M ammonium buffer, *p*H 9, and the total volume was made to 10 cc. with water. In the control experiment, water replaced lanthanum hydroxide.

Dephosphorylation of Casein.—Casein was not dephosphorylated at room temperature, 25°, as Bamann has shown (1). But at 70°, the catalytic effect of lanthanum hydroxide was observed (Table 4).

Summary

1. The dephosphorylation reaction of RNA by lanthanum hydroxide gel was further studied. The activation energy of the reaction is 20,200~20,400 cal. Optimal *p*H is between 8 and 9.

2. RNA is hydrolysed almost completely into nucleosides and inorganic phosphate at 90° in 40 hours at *p*H 8. The formation of nucleosides as the final product of hydrolysis was shown from the reducing power measurements and periodate consumption of products.

3. DNA is not dephosphorylated at all under conditions where RNA is almost completely dephosphorylated. This may be related to the structural difference of DNA and RNA.

4. Preparative method for ribonucleosides from RNA under catalytic effect of lanthanum hydroxide was described. Ribonucleosides are obtained in good yields.

5. Desoxyribo-, a-ribo-, b-ribo-, and 5′-ribocytidylic acid are all subject to catalytic dephosphorylation. 5′-Ribocytidylic acid is dephosphorylated most slowly.

6. Cerium hydroxide can be used as catalyst of the reaction in the same way with lanthanum hydroxide.

7. The dephosphorylation of casein is considerably accelerated by lanthanum hydroxide at 70° but not at 25°.

Part of the cost of this investigation was defrayed from the Scientific Research Encouragement Grant from the Ministry of Education.

Chemical Institute, Faculty of Science, Nagoya University

Polarographic Behavior of Cinnamic-, Styrylacetic- and Crotonic- Acids[1]

By Shin-ichi Ono and Tadao Hayashi

(Received December 20, 1952)

Introduction

Several authors have already measured the reduction potentials of cinnamic acid[2] and crotonic acid[3] in various solutions.

In connection with the electrolytic reduction of cinnamic acid,[4] the authors have undertaken the polarographic observation of cinnamic-, styrylacetic- and crotonic acids, in order to know the relation between the reducibility and the structure of molecules and also the reduction of carbon-carbon double bond in these acids at a dropping mercury electrode.

Experimental

Dioxane-water mixture containing 50% dioxane was used as a solvent, with several types of supporting electrolytes. Since the decomposition potential of buffer-solutions was found to be less negative than the reduction potential of the double bond in these acids, special care was taken for the selection of supporting electrolytes. In the experiments which will be discussed, unbuffered electrolytes were usually used. The supporting electrolytes used were as follows:

(a) Acid media
  (1) HCl—0.1N LiCl System
  (2) HCl—0.1N $SrCl_2$ 〃
  (3) HCl—0.1N $CaCl_2$ 〃

(b) Neutral media
  (1) $(CH_3)_4NBr$ (0.1N), $(CH_3)_4NI$ (0.05N)
  (2) LiCl. KCl, NaCl, NH_4Cl (0.1N)
  (3) $CaCl_2$, $SrCl_2$, $BaCl_2$ (0.1N)

(c) Alkaline media
  (1) LiOH (0.1N)

The dropping mercury electrode had the following characteristics. At a pressure of 50 cm of mercury, the droptime in 50% Dioxane-0.1N $(CH_3)_4NBr$ was 3.98 sec. (Open circuit). The value of m was 1.01 mg. sec.$^{-1}$, with a calculated value of $m^{2/3}t^{1/6}$ of 1.267 mg.$^{2/3}$t$^{-1/2}$ (Open circuit).

Table 1

Half-wave Potentials and Diffusion Currents of Polarographic Waves of Styrylacetic and Crotonic Acids. (50% Dioxane)

Sample (mol.)	Electrolyte	Half-wave Potential (volt vs. S. C. E.)	I_l (μA.)	I_l/C.
Styrylacetic acid				
4×10^{-3}	0.1N $(CH_3)_4NBr$	−1.70	4.56	1.14
1 〃	〃	−1.64	1.06	1.06
2 〃	0.05N $(CH_3)_4NI$	−1.69	2.40	1.20
1 〃	〃	−1.64	1.16	1.16
2 〃	0.1N LiCl	−1.65	2.40	1.20
2 〃	0.1N $SrCl_2$	−1.64	2.80	1.40
2 〃	0.1N $CaCl_2$	−1.60	2.20	1.10
2 〃	0.1N LiOH	—		
Crotonic acid				
5×10^{-3}	0.1N $(CH_3)_4NBr$	−1.73	9.12	1.82
2 〃	〃	−1.70	3.38	1.69
2 〃	0.1N LiCl	−1.66	3.04	1.52
2 〃	0.1N $SrCl_2$	−1.65	2.72	1.31
2 〃	0.1N LiOH	—		

(1) This paper was presented at the Annual meeting of the Chemical Society of Japan, held in Tokyo, on April 1952. This paper shall be "Part IV of Electrolytic Reduction of Aromatic Carboxylic Acids".

(2) (a) L. Schwaer, *Collection Czechoslov. Chem. Commun.*, **7**, 326, (1935).
(b) G. Semerano and A. Chisini, *Gazz., Chim. Ital.*, **66**, 510, (1936).
(c) S. Wauzonek, S. C. Wang and P. Lyons, *J. Org. Chem.*, **15**, 593, (1950).

(3) (a) K. Shoji, *Sc. P. (Japanese)*, **9**, 69, (1930).
(b) M. v. Stackelberg and W. Stracke, *Z. Elektrochem.*, **53**, 118, (1949).

(4) S. Ono and T. Hayashi, This Bulletin, **26**, 11, (1953).

The electrolytic cell was a simple cylindrical shape with a mercury pool anode, and was provided with side arms for anode connection and for admission of hydrogen for the removal of dissolved oxygen.

The anode potential was measured against a saturated calomel electrode (S.C.E.). The current-voltage curve was photographically recorded with A Model SH Shimazu Polarograph, which has a current scale calibrated in microamperes (Sensibility; 8.0×10^{-3}microamp./mm./m.). All the experiments were carried out at room temperature. ($15°\pm1°C$).

All samples were prepared by the usual method, and purified by recrystallization. Cinnamic acid, m.p. 133—133.5°C, styrylacetic acid, m.p. 87—87.5°C, crotonic acid, m.p. 71—72°C.

Dioxane was purified by refluxing with sodium for 12 hours and by distillation.

The purified samples were dissolve in dioxane to the concentration of 1×10^{-2}mol/l, as a stock solution.

Polarographic results

(1) **Electroreduction in neutral and alkaline solutions.**—Both styrylacetic acid and crotonic acid gave a single wave, corresponding to the deposition of hydrogen ion in neutral solution, whereas they gave no polarographic (reduction) wave in alkaline solution. Table 1 shows the observed half-wave potentials and diffusion currents of styrylacetic and crotonic acids.

On the other hand, cinnamic acid gave a well-defined two-step polarographic wave in neutral solutions, and the first wave diminished by the addition of alkali.

Typical polarograms are given in Fig. 1, using a 0.05N $(CH_3)_4NI$ solution as a supporting electrolyte.

Table 2 shows a summary of the observed half-wave potentials and diffusion currents of cinnamic acid. In the presence of NH_4Cl, KCl, or NaCl as a supporting electrolyte, the second wave of cinnamic acid overlapped the decomposition potentials of these cations; therefore, it was difficult to distinguish "the real reduction wave" of the carbon-carbon double bond. However, if we used solutions of LiCl, $SrCl_2$, $CaCl_2$, $(CH_3)_4NI$, or $(CH_3)_4NBr$, as a supporting electrolyte, cinnamic acid gave a well-defined two-step reduction wave.

It was an interesting fact that the half-wave potentials of the second wave became more positive by 0.12 volt for $SrCl_2$ and by 0.15 volt for $CaCl_2$ than those for $(CH_3)_4NBr$.

We found, when $(CH_3)_4NBr$ was used, that the half-wave potentials of cinnamic acid were independent of the concentration of cinnamic acid,

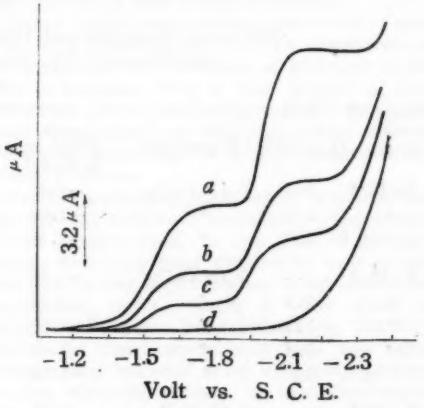

Fig. 1.—A typical polarograme of Cinnamic acid in 0.05 N $(CH_3)_4NI$ (containing 50% Dioxane, 0.001% gelatine)
(a) 4×10^{-2}M. of sample. (b) 2×10^{-3}M. (c) 1×10^{-3}M. (d) Residual Current.

Table 2

Half-wave Potentials and Diffusion Currents of Cinnamic Acid in Neutral or Alkaline Solution. (50% Dioxane, with 0.001% gelatin)

Cinnamic acid ($mol.\times10^{-3}$)	Electrolyte	First wave			Second wave		
		$\pi_{1/2}$ (Volt vs. S. C. E.)	I_l (μA.)	$I_l/C.$	$\pi_{1/2}$ (Volt vs. S. C. E.)	I_d (μA.)	$I_d/C.$
5.0	$(CH_3)_4NBr$	−1.53	5.76	1.15	−2.03	9.28	1.86
4.0	〃	−1.52	4.08	1.02	−2.02	7.20	1.80
2.0	〃	−1.50	2.16	1.08	−2.01	3.68	1.84
1.0	〃	−1.49	1.05	1.05	−1.98	1.85	1.85
4.0	$(CH_3)_4NI$	−1.56	4.16	1.04	−2.05	6.88	1.72
2.0	〃	−1.52	2.16	1.08	−2.01	3.52	1.76
1.0	〃	−1.55	1.10	1.10	−1.99	1.78	1.78
2.0	LiCl	−1.54	2.24	1.12	−1.99	5.84	2.92
2.0	$SrCl_2$	−1.55	2.40	1.20	−1.89	3.52	1.76
2.0	$CaCl_2$	−1.53	2.24	1.12	−1.86	3.52	1.76
4.0	LiOH	—			−1.97	11.00	2.75
2.0	〃	—			−1.96	5.40	2.70
1.0	〃	—			−1.95	2.80	2.80

and the height of waves increased linearly with the concentration.

It was made clear that lithium cinnamate gave a single wave corresponding to the reduction of cinnamate anion, by using 0.1N LiOH solution.

(2) **Electroreduction in acid solution.**—In the case of 0.1N HCl solution as a supporting electrolyte, cinnamic-, styrylacetic- and crotonic-acids gave no reduction waves of carbon-carbon double bond, owing to the decomposition potential of hydrogen ion in the bulk of HCl solution. (Decomposition potential of hydrogen ion was measured at ca. −1.16 volt. vs. S. C. E.)

Another attempt was made to investigate the polarographic behavior of cinnamic acid in some unbuffered acid solutions.

Table 3 shows a summary of the observed half-wave potentials and diffusion current of cinnamic acid in acid solution. The second wave (I_d) which corresponds to the reduction of carbon-carbon double bond, was diminished linearly with the increase of the concentration of HCl, while the first wave (I_l) grew remarkably large, owing to the decomposition of hydrogen ion.

(3) **Electroreduction of ethyl cinnamate.**—We have undertaken the polarographic observation of ethyl cinnamate in neutral and also alkaline solutions.

Ethyl cinnamate gave a single wave which might correspond to the reduction of carbon-carbon double bond in a neutral solution (0.1N $(CH_3)_4NBr$), whereas it gave a double wave in

Table 3

Half-wave Potentials and Diffusion Currents of Cinnamic Acid in Acid Solution. (50% Dioxane, 0.004—0.005% gelatin)

Cinnamic acid (mol.)	HCl (N.×10⁻³)	Electrolyte	First wave $\pi_{1/2}$ (Volt vs. S. C. E.)	First wave I_l (μA.)	First wave I_l/C.	Second wave $\pi_{1/2}$ (Volt vs. S. C. E.)	Second wave I_d (μA.)	Second wave I_d/C.
2×10^{-3}	0.5	0.1N $CaCl_2$	−1.55	3.2	1.60	−1.89	2.9	1.45
〃	1.0	〃	−1.50	4.5	2.25	−1.89	1.5	0.75
(c. f.	1.0	〃	−1.47	2.5)				
5×10^{-3}	—	0.1N $CaCl_2$	−1.55	5.2	1.04	−1.87	7.8	1.54
〃	0.5	〃	−1.55	6.0	1.20	−1.87	6.8	1.36
〃	1.0	〃	−1.50	7.2	1.44	−1.88	5.8	1.16
〃	5.0	〃	−1.49	22.2	4.44	−1.77	3.4	0.68
(c. f.	5.0	〃	−1.53	24.4)				
5×10^{-3}	—	0.1N $SrCl_2$	−1.55	5.4	1.08	−1.90	9.4	1.88
〃	0.5	〃	−1.54	6.4	1.28	−1.90	8.6	1.72
〃	1.0	〃	−1.50	8.2	1.64	−1.92	7.4	1.28
〃	5.0	〃	−1.47	25.4	5.08	−1.79	5.6	1.12
(c. f.	5.0	〃	−1.51	25.5)				
1×10^{-2}	—	0.1N $SrCl_2$	−1.57	12.8	1.28	−1.97	18.0	1.80
〃	1.0	〃	−1.54	14.8	1.48	−1.96	16.4	1.64
〃	2.0	〃	−1.53	20.4	2.04	−1.97	13.2	1.32
〃	5.0	〃	−1.48	33.2	3.32	−1.86	10.4	1.04
〃	10.0	〃	−1.47	99.6	9.96	−1.86	6.8	0.68
(c. f.	1.0	〃	−1.55	3.2)				

Table 4

Half-wave Potentials and Diffusion Currents of Ethyl Cinnamate. (50% Dioxane)

Sample (mol.)	Electrolyte	First wave* $\pi_{1/2}$ (Volt vs. S. C. E.)	First wave* i_d (μA.)	Second wave $\pi_{1/2}$ (Volt vs. S. C. E.)	Second wave i_d (μA.)
5×10^{-3}	0.1N $(CH_3)_4NBr$	−1.69	13.1	—	—
1×10^{-3}	〃	−1.68	2.6	—	—
4×10^{-3}	0.1N LiOH	−1.65	.....**	−1.97	.....**
2×10^{-3}	〃	−1.66	.....	−1.96	.....
1×10^{-3}	〃	−1.67	.....	−1.96	.....

* This first waves have different meaning for those of Table 2.

** i_d value are omitted, because they are changeable with the lapse of hydrolysis.

alkaline solution (0.1N LiOH).

Table 4 gives the observed half-wave potentials and diffusion currents of ethyl cinnamate. Comparing the results obtained from both cinnamic acid and its ester in the same supporting electrolyte, it was clear that the half-wave potential of ethyl cinnamate was more positive than that of cinnamic acid. The appearance of the double wave in the reduction of the ethyl cinnamate in alkaline solution can be attributed mainly to the reduction of two different forms, that is, ethyl cinnamate and cinnamic acid resuling from

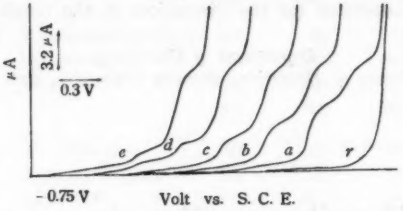

Fig.—2.—A polarogram for the hydrolysis of Ethyl Cinnamate. (Supporting media: 50% Dioxane 0.1N LiOH, Sample: 1.5×10^{-3}M.) (R) Residual Current. (a) Initial state, (b), (c), (d), (e) states after the lapse of respectively 40 min., 80 min., 120 min., 160 min., from (a).

hydrolysis. Fig. 2 shows a polarograme for the hydrolysis of ethyl cinnamate. The first wave was observed to have diminished by the hydrolysis. The total wave heights were constant and they were twice as large as the height of cinnamic acid in the same concentration. Detailed discussion on this phenomenon will be presented in another paper.

Discussion

It has been pointed out that the electroreducibility of a carbon-carbon double bond was closely related to the nature of the conjugated system of the double bond in the study of polarographic reduction of several unsaturated acids.[2a]

It was found in the present experiment that cinnamic acid gave only the polarographic wave corresponding to the reduction of carbon-carbon double bond. The electroreduction of cinnamic acid gave two-step polarographic waves in neutral solution. Under these conditions, there would be neutral molecules, dissociated cinnamate anions and hydrogen ions in the vicinity of the electrode surface and these species would contribute to the potential determining step. The following characteristic kinds of behavior were observed;

(1) Well-defined two-step reduction wave was obtained in a neutral solution.

(2) The first wave was observed to diminish by addition of alkali.

(3) Lithium cinnamate gave a single wave either in neutral or in alkaline solution.

(4) The heights of the first wave and the heights of the second wave were both proportional to the concentration of samples.

(5) Total wave heights of both the first and the second waves remained constant when alkali was introduced into a neutral solution.

In the initial stage of waves (first wave), therefore, this phenomenon may be considered as being due to the discharge of hydrogen in the bulk of solution. This is true because at such pH values (pH>6) the concentration of the undissociated acid becomes negligibly small and the cinnamate anion may be reduced directly on the electrode surface.

Another interesting result which was obtained was that the half-wave potentials of the carbon-carbon double bond, in the case of divalent cations as a supporting electrolyte, were shifted and became less negative than in the case of the monovalent cation. (Table 5) The effect of divalent cations can be explained by the ionic activity of these cations that form the metal complex with carbonyl anion and tend to diffuse to the electrode surface by the electrostatic interaction.

It has been mentioned that[4] the electrolytic reduction of cinnamic acid in acid solution with mercury cathode, gave rise to bimolecular compounds, which were produced by the dimerization of free radicals, Ph-$\dot{C}$HCH$_2$COOH obtained from cinnamic acid. But in alkaline solution, no bimolecular compounds were produced; that is, only hydrocinnamic acid was given.

If we assume that the polarographic reduction process will take place in the same manner as in the case of so-called electrolytic reduction, it may be expected that there will be considerable change in the polarograms obtained from acid

Table 5

Effect of Cations on the Half-wave Potentials of Cinnamic acid. (50% Dioxane)

Sample (2.0×10^{-3} mol.)	Cation	Electrolyte	Half-wave Potential (Volt vs. S. C. E.)	I_d (μA.)	I_d/C.
Li cinnamate	$(CH_3)_4N^+$	0.1N $(CH_3)_4NBr$	−1.98	6.0	3.00
〃	Li^+	0.1N LiCl	−1.93	8.5	4.25
〃	Sr^{++}	0.1N $SrCl_2$	−1.88	5.8	2.90
〃	Ca^{++}	0.1N $CaCl_2$	−1.84	5.5	2.75
Ba cinnamate	Ba^{++}	0.1N $(CH_3)_4NBr$	−1.92	5.8	2.90
Ca cinnamate	Ca^{++}	〃	−1.90	5.7	2.85

solution, compared with that in neutral or alkaline solution. But, in the present experiments, no clear effect of hydrogen ion concentration could be established, since the half-wave potential of carbon-carbon double bond was observed to be more negative than the decomposition potential of hydrogen ion.

Summary

1) In neutral solution, both styrylacetic acid and crotonic acid gave a single wave (ca. —1.6—-1.7 *v.*), on the other hand cinnamic acid gave a well-defined two-step polarographic wave (ca. —1.5 *v.* and ca. —2.0 *v.*) corresponding to the reduction of carbon-carbon double bond. The half-wave potentials of cinnamic acid were shifted by the presence of divalent cations.

2) Ethyl cinnamate gave a single wave (ca. —1.7 *v.*) in neutral solution, but in alkaline solution it gave two waves (ca. —1.7*v.* and ca. —2.0 *v.*). The first wave was observed to diminish by the hydrolysis in alkaline solution.

The authors wish to express their thanks to Dr. I. Tachi of the Univ. of Kyoto, and his collaborator for the discussion of the results.

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Dipole Moments of Tropone, 2-Phenyltropone, Tropolone Methyl Ether and their Derivatives*

By Yukio KURITA, Shuichi SETO, Tetsuo NOZOE and Masaji KUBO

(Received December 23, 1952)

Hitherto we studied the dipole moments of tropolone (or cycloheptatriene-ol-2-one-1) and its derivatives.[1~5] The characteristic feature of the molecules of these compounds is that the electronic structures with a negative charge at the carbonyl oxygen and a positive charge at one of the carbon atoms in the ring contribute appreciably to the normal state. The same situation is expected[6~8] for tropone (or cycloheptatrienone), one of the simplest and the most fundamental compounds with a cycloheptatriene ring. The determination of the dipole moment of tropone made in the present investigation will throw light on the theory of the π-electron problem as applied to the charge distribution in this molecule.

We have also carried out measurements on the dipole moments of eleven of its derivatives. All the compounds studied were synthesized* and purified by one of us (T.N.) and his collaborators at the laboratory of organic chemistry, Tôhoku University.

Experimental Method and Results

All the measurements were made in benzene solution at 25° except in one case (compound VII) for which the temperature was varied from 20° to 40°. The apparatus and the method of measurement were the same as used in our earlier works. The Halverstadt-Kumler's method was employed throughout. The moment of tropolone was remeasured, in view of its importance, to get more accurate value from data at various concentrations. The results are shown in Tables 1 and 2, where the same notations are used as those in the previous reports.

Discussion of Results

Tropone.—The value 4.17 D for the moment of tropone is in fair agreement with that of Giacomo and Smyth, 4.30 D.[10] The large-

* Read before the scientific meeting of the Chemical Society of Japan (A Symposium on Tropolone Chemistry) held on July 5, 1952.

(1) Y. Kurita, T. Nozoe and M. Kubo, This Bulletin, **24**, 10 (1951).

(2) Y. Kurita and M. Kubo, ibid., **24**, 13 (1951).

(3) Y. Kurita, T. Nozoe and M. Kubo, ibid., **24**, 99 (1951).

(4) Y. Kurita, T. Nozoe and M. Kubo, ibid., **26**, 242 (1953).

(5) Y. Kurita, T. Mizuno, T. Mukai and M. Kubo, ibid., **26**, 192 (1953).

(6) T. Nozoe, T. Mukai, K. Takase and T. Nagase, *Proc. Japan Acad.*, **28**, No. 9, 477 (1952).

(7) H. J. Dauben and H. J. Ringold, *J. Am. Chem. Soc.*, **73**, 876 (1951).

(8) W. von E. Doering and F. L. Detert, ibid., **73**, 876 (1951).

* See literatures at the end of Table 1.

(10) A. D. Giacomo and C. P. Smyth, *J. Am. Chem. Soc.*, **74**, 4411 (1952).

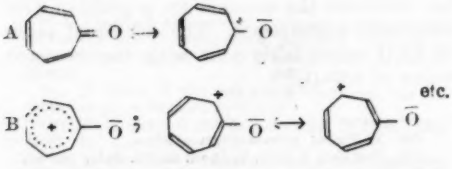
Table 1

Dielectric Constant and Density Increments, 25°

	Compounds	$w\times10^5$	$\Delta\varepsilon\times10^4$	$\Delta d\times10^5$
I	Tropone[a]	208	439	46
	b. p. 84—85°(6 mm.)	439	862	100
		737	1364	154
		1070	1998	224
II	2-Phenyltropone[b]	225	225	—
	m. p. 85—86°	380	—	79
		804	760	192
		1184	1087	267
III	4-Bromo-2-phenyl-tropone[c]	151	60	21
		366	99	101
	m. p. 88°	627	195	196
		841	289	290
IV	3,7-Dibromo-2-phenyltropone[d]	331	156	113
		470	223	182
	m. p. 118°	842	387	351
		1328	611	575
V	2-(*p*-Methoxy-phenyl)-tropone[e]	317	269	73
		506	416	105
	m. p. 54.5—55.0°	875	670	244
VI	Tropolone methyl ether[f]	341	538	80
		612	1065	149
	(oil)	1119	1941	278
VII	(Tropolone methyl ether)$_2$·H_2O,[f]		m. p. 41°	
	20°	253	438	—
		358	650	45
		558	993	105
	30°	253	411	65
		358	608	98
		558	930	142
	40°	253	366	10
		358	555	86
		558	874	168
VIII	*o*-Bromotropolone methyl ether A	160	242	67
		252	393	107
	(7-Bromo-2-methoxy-tropone)[g]	335	514	141
		563	876	239
	m. p. 91—91.5°	1077	1670	488
IX	*o*-Bromotropolone methyl ether B	319	187	113
		613	356	263
	(3-Bromo-2-methoxy-tropone)[g]	1081	589	430
	m. p. 76—77°	1490	867	637
X	α-Thujaplicin methyl ether B[h]	483	430	80
		694	710	120
	m. p. 72°	1224	1250	210
XI	*m*-Methyltropolone methyl ether A	200	320	48
		297	543	84
	(6-Methyl-2-methoxy-tropone)[i]	527	891	135
	m. p. 95.5-96°	627	1160	168
XII	Tropolone[j]	471	578	114
	m. p. 51°	864	993	227
		1187	1361	309
		1911	2206	488
		2378	2705	613

(a) T. Nozoe, T. Mukai, K. Takase and T. Nagase, *loc. cit.* reference (6).
(b) T. Nozoe, T. Mukai and J. Minegishi, *Proc. Japan Acad.*, **27**, 419 (1951).
(c) T. Nozoe, S. Seto and S. Ito, ibid., to be published shortly.
(d) T. Nozoe, T. Mukai and I. Murata, ibid., **28**, 142 (1952).
(e) T. Nozoe, S. Seto, T. Ikemi and T. Sato, ibid., **28**, No. 8, 413 (1952).
(f) T. Nozoe, S. Seto, T. Ikemi and T. Arai, ibid **27**, 102 (1951).
(g) T. Nozoe, Y. Kitahara and S. Masamune, ibid., **27**, 649 (1951).
(h) T. Nozoe, Y. Kitahara, K. Yamane and T. Ikemi, ibid., **27**, 193 (1951).
(i) P. Akroyd, R. D. Haworth and J. D. Hobson, *J. Chem. Soc.*, **1951**, 3427.
(j) T. Nozoe, S. Seto, Y. Kitahara, M. Kunori and Y. Nakayama, *Proc. Japan. Acad.*, **26**, No. 7, 38 (1950).

increase, about 1.1 D, in the moment of this molecule over that of cycloheptanone, 3.04D,[11] indicates the importance of the contribution of polar structure B.



Sutton[12] pointed out that the moments of various unsaturated ketones and aldehydes with conjugated C=C double bonds fit in well with calculated values, if we give mesomeric moments of 0.1 D and 0.2 D respectively to C—C bonds adjacent to the carbonyl group and to the next C=C bonds, each lying along its respective bond. The correction of mesomeric effect can only partly explain the increase of moment of tropone over that of cycloheptanone. The calculated value is 3.5D, still smaller than the observed value by an amount of 0.7 D. This may be attributed to an additional effect due to the formation of cycloheptatrienone ring. In fact, the difference

(11) Hs. H. Günthard and T. Gäumann, *Helv. Chim. Acta.*, **34**, 39 (1951).

(12) J. B. Bentley, K. B. Everard, R. J. B. Marsden and L. E. Sutton, *J. Chem. Soc.*, **1949**, 2957.

Table 2

Dipole Moments of Tropone and Related Compounds in Benzene Solution at 25°

Compounds		ε_1	d_1(g./cc.)	α	β(g./cc.)	$P_{2\infty}$(cc.)	R_D(cc.)	μ(D)
I		2.2788	0.87121	17.98	0.204	387± 4	30.9[a]	4.17±.03
II		2.2751	0.87144	9.01	0.234	355± 8	55.1	3.82±.05
III		2.2719	0.87075	3.36	0.387	215±12	62.9	2.73±.11
IV		2.2732	0.87078	4.54	0.461	346±12	70.7	3.67±.01
V		2.2772	0.87084	7.15	0.316	332± 9	61.4	3.63±.05
VI		2.2668	0.87127	17.92	0.254	494± 1	37.2	4.72±.01
VII	20°	2.2816	0.87605	18.06	0.300	1045±29	78	6.81±.10*
	30°	2.2617	0.86616	16.88	0.246	1005±26	78	6.78±.10*
	40°	2.2384	0.85443	16.55	0.502	980±26	78	6.80±.10*
VIII		2.2721	0.87124	15.56	0.458	666± 2	45.0	5.51±.01
IX		2.2724	0.87112	5.71	0.436	269±11	45.0	3.31±.08
X		2.2716	0.87156	10.34	0.165	397± 4	51.1	4.11±.02
XI		2.2683	0.87131	18.67	0.272	565±21	41.7	5.06±.10
XII		2.2759	0.87113	11.26	0.258	289± 3	32.5[b]	3.53±.02

(a) R_D observed is 33.9 cc.[8]

(b) R_D observed is 37.46 cc. and the value extrapolated to infinite wavelength is 34.30 cc.[9]

* Apparent moments.

of 0.7 D is very close to the moment of 0.85D calculated theoretically for heptafulvene.[13] The magnetic susceptibility measurements by Maruha and Hazato[14] also indicate the importance of the electronic structures of the type B.* If we assume that the structure A has a moment 3.0 D and the structure B has 16.8 D, the contribution x of the polar form B can be calculated from

$$3.0(1-x)+16.8\,x=4.17$$

as $x=0.082$. There are six individual structures for B. Hence the contribution of each polar structure is 0.014, giving an effective positive charge 0.014 e to each of the six ring carbon atoms. Brown[15] in his molecular orbital treatment gave an effective charge of 0.06—0.11 e. This is not surprising, since the neglect of mutual repulsion between electrons, made in simple molecular orbital method, will always give too high value for the theoretical moment.

2-Phenyltropone and its derivatives.— The moment of 2-phenyl-tropone is smaller than that of tropone, due to the induction effect. Presumably the benzene ring is nearly perpendicular to the plane of cycloheptatriene ring to minimize steric hindrance. The absorption spectra studied by Tsuboi[16] also indicate that the degree of conjugation between the two rings is not great. With the assumption that the cycloheptatriene ring has a regular heptagon form, that the moment of 2-phenyltropone, 3.82 D in magnitude, lies along the C=O bond direction and that the value of C—Br bond moment is 1.5 D, the moment of 4-bromo-2-phenyltropone was calculated to be 2.6 D, a little lower than the observed value of 2.73 D. Actually owing to induction effect, the moment of 2-phenyltropone makes an angle of a few degrees with the C=O direction towards phenyl-group. This with C—Br moment gives a greater resultant moment in agreement with experiment. The moment calculated for 3,7-dibromophenyltropone in a similar manner is 4.4 D to be compared with the observed value of 3.67 D. The difference of this order of magnitude may be attributed to the induction and steric effects.

The position of methoxy-group in 2-(*p*-methoxyphenyl)-tropone has already been determined by us[17] from evidences in organic synthesis. Hoping to confirm the conclusion, we calculated the moment for *p*-position with reasonable assumptions. The calculated value of 3.9 D agrees fairly well with the observed value of 3.63 D.**

(9) T. Shiratori and S. Kinumaki, private communication.

(13) E. D. Bergmann, E. Fischer, D. Ginsberg, Y. Hirshberg, D. Lavie, M. Mayot, A. Pullman and B. Pullman, *Bull. Soc. Chim. France*, **1951**, 684.

(14) J. Maruha and G. Hazato private communication.

* See also the literature (a) of Table 1.

(15) R. D. Brown, *J. Chem. Soc.*, **1951**, 2670.

(16) M. Tsuboi, private communication.

(17) T. Nozoe, S. Seto, T. Ikemi and T. Sato, *loc. cit.* reference (e) of Table 1.

** The theoretical value is rather insensitive to the presumed position of methoxy-group (3.9 D for *para*, 3.9 D for *meta* and 3.4 D for *ortho*-substitution). It is therefore impossible from the dipole moment data alone to determine the position.

Table 3

Dipole Moments of Methyl Ethers of Tropolone Derivatives

2-Methoxy-tropones	*cis*-Position	Perpendicular form	*trans*-Position	Observed (D)
3-Bromo-	3.4—4.4	4.1—4.9	4.7—5.4	3.31
7-Bromo-	4.0—4.6	5.3—5.7	6.3—6.7	5.51
6-Methyl-	3.3—4.2	4.3—5.0	5.1—5.7	5.06
7-Isopropyl-*	2.9—3.8	3.8—4.6	4.6—5.2	4.11

Tropolcne methyl ether and its derivatives.—The moment of tropolone methyl ether was estimated from those of tropone and methoxy-group with due regard to the mesomeric moments of O—C (ring) bond. The calculated moment is 3.1—3.9 D for *cis*-configuration, i.e., for methyl group near the oxygen atom of C=O in the ring plane, 5.1—5.6 D for *trans*-configuration and 4.2—4.8 D for the structure in which the methoxy-group lies in a plane perpendicular to the ring. The possible explanation of the observed moment, 4.72 D, is either that the methoxy-group is out of the ring plane to minimize steric hindrance or that both *cis*- and *trans*-configurations are present to give an intermediate moment. A similar conclusion can also be derived for substituted methoxytropones as shown in Table 3.

In particular, the moment of 3-bromo-2-methoxytropone is very close to the theoretical value for *cis*-configuration. Probably the methoxy-group is repelled by the great steric repulsion of bromine atom at 3-position. This will render the molecule less stable than that of 7-bromo-2-methoxytropone in good agreement with the fact that the former is more liable to aromatization than the latter.[18] Mills and Tyrell[19] in their preliminary measurements gave for the moment of *m* (β in their notation)-methyltropolone methyl ether A the value of 4.9 D in agreement with ours. Sutton and Saxby[20] also measured the moment** of this compound and supported the constitutions proposed by Akroyd and others.

The moment of tropolone methyl ether hydrate is independent of temperature and the dependence of the dielectric constant and density of the solution upon concentration is normal. This fact suggests no association taking place. The observed apparent moment of 6.80 D agrees within experimental errors with

$$\bar{\mu}=[2\mu^2(\text{trop. meth. eth.})+\mu^2(H_2O)]^{1/2}$$
$$=(2\times4.72^2+1.75^2)^{1/2}=6.9\text{ D}.$$

Hence we conclude that in benzene solution the hydrate dissociates into three separate molecules.

Summary

The dipole moments of tropone, 2-phenyltropone, tropolone methyl ether and their derivatives were measured in benzene solution at 25°. The increase of moment of tropone over that of cycloheptanone was adequately explained by mesomeric effect and an additional effect due to the formation of cycloheptatriene ring. The latter effect was supported by the theoretical moment for heptafulvene. The moments of various derivatives were compared with the theoretical data. The agreement between them confirmed the correctness of the position of substituents in these compounds already determined or inferred from the standpoint of organic syntheses. The apparent moment of tropolone methyl ether hydrate indicates that in benzene the hydrate dissociates into three separate molecules.

We wish to express our thanks to Mr. Y. Kitahara and Mr. T. Mukai of Tôhoku University for their collaboration in the syntheses of these compounds. Our thanks are also due to the Ministry of Education in aid of this research.

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* The position of isopropyl-group was determined by T. Nozoe, S. Seto, T. Ikemi and T. Sato from evidences in organic chemistry, the details of which will be published shortly.

(18) T. Nozoe, Y. Kitahara and S. Masamune, *loc. cit.* reference (g) of Table 1.

(19) R. D. Haworth and J. D. Hobson, *J. Chem. Soc*, **1951**, 561.

(20) P. Akroyd, R. D. Haworth and J. D. Hobson, *loc. cit.* reference (i) of Table 1.

** Unfortunately their value is not given in the paper.

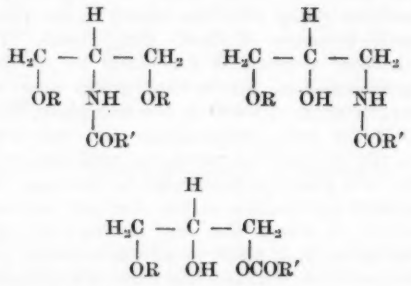
Derivatives of dl-Aminopropanediols*

By Chieko URAKAMI and Kasumi KAKEDA

(Received January 9, 1953)

Since the structure of chloramphenicol was proven[1] by a group of workers at the laboratories of Parke Davis & Co. to be *D*-(levo)-threo-2-dichloroacetamido-1-*p*-nitrophenyl-1, 3-propanediol, a number of papers dealing with the preparation of its analogs have appeared, but esterification of the hydroxyl groups of the chloramphenicol type compounds have not been attempted. It might be possible to maintain bacteriostatic activity by dropping off the *p*-nitrophenyl group from the chloramphenicol molecule and by esterifying the hydroxyl groups with *p*-nitrobenzoic or fatty acids of varied chain lengths since certain esters of glycerol[2] have been reported to be active against *Mycobacterium tuberculosis*. As far as we are aware, there have been reported no cases where the haloacylaminopropanediols have been esterified with the acids we used in this experiment.

A number of functional derivatives of the following three types of compounds were prepared (Table 1, 2 and 3).



R=H or acyl group,
R′=haloalkyl group

1- and 2-Aminopropanediols were prepared

Teble 1

1-Aminopropanediol Series, $CH_2(OR)CH(OH)CH_2NHCOCHCl_2$

No.	R	M. P. °C	$n_D^{18.5}$	Calcd. C	Calcd. H	Calcd. N	Found. C	Found. H	Found. N
I	H	59.0—59.5		29.70	4.49	6.93	29.17	4.29	6.78
II	$C_8H_{17}CO$	55.5—56.5 (from absol. MeOH)		49.13	7.36	4.09	48.90	7.70	4.13
III	$C_{11}H_{23}CO$	70.5—71.0 (〃)		53.12	8.13	3.64	53.32	8.36	3.41
IV	p-$O_2NC_6H_4CO$	138.0—138.5 (〃)		41.04	3.44	7.98	41.44	4.01	7.67
V	i-C_3H_7CO	155—170/1.5×10⁻⁴mm.Hg.*	1.492	39.70	5.51	5.15	38.28	5.08	5.39
VI	i-C_4H_9CO	150—170/8×10⁻⁴mm.Hg.*	1.486	41.98	5.99	4.89	43.76	5.91	5.08

* Bath temperature.

Reaction Condition

No.	Reaction time	Yield%	Solubility: MeOH	EtOH	AcMe	Et_2O	AcOH	AcOEt	$CHCl_3$	C_6H_6	Petr. ether	H_2O
II	20 hrs.	27	+	+	+	+	+	+	−	−	−	−
III	24 hrs.	43	+	+	+	+	+	+	+	+ (hot)	+ (hot)	−
IV	2 weeks	34	+	+	+	−	+	+	+ (hot)	−	−	−
V	24 hrs.	58	+	+	+	+		+	+	−	+ (hot)	−
VI	24 hrs.	65	+	+	+	+		+	+	−	+ (hot)	−

* Part of this work was presented at the Fifth Annual Meeting of the Chemical Society of Japan, April 1952.

(1) M. C. Rebstock, H. M. Crooks, Jr., and J. Controulis, *J. Am. Chem. Soc.*, **71**, 2458, 2463 (1949).

(2) Th. Wagner-Jauregg and H. Arnold, *Ber.*, **70**, 1459 (1937); H. Arnold, ibid., **71**, 1505 (1938); ibid., **73**, 90 (1940).

Table 2

2-Aminopropanediol Series, $CH_2(OR_1)CH(NHCOCHCl_2)CH_2(OR_2)$

No.	R_1	R_2	M. P. °C.*	Calcd. C	Calcd. H	Calcd. N	Found. C	Found. H	Found. N
VII	H	H	143.5—144.0	29.70	4.49	6.93	30.25	5.97	6.84
VIII	$C_8H_{17}CO$	$C_8H_{17}CO$	50.0—51.0	57.24	8.56	2.90	58.34	8.27	2.82
IX	$C_{11}H_{23}CO$	$C_{11}H_{23}CO$	68.5—69.0	61.04	9.42	2.23	60.90	9.22	2.47
X	p-$O_2NC_6H_4CO$	H	141.0—142.0	41.04	3.44	7.98	41.49	3.34	7.67
XI	$C_{15}H_{31}CO$	$C_{15}H_{31}CO$	80.0—81.0	65.46	10.24	2.06	66.21	10.04	2.21
XII	$C_{17}H_{31}CO$	$C_{17}H_{31}CO$	80.0—80.5	66.99	10.56	1.90	67.97	10.39	1.99

* Recrystallized from abs. EtOH.

No.	Reaction time	Yield%	Solubility: MeOH	EtOH	AcMe	Et_2O	AcOH	AcOEt	$CHCl_3$	C_6H_6	Petr. ether	H_2O
VIII	3 days	83 (crude)	+	+	+	+			+	−	−	−
IX	3 days	83 (crude)	+	+	+	+			+	−	−	−
X	5 days	73 (crude)	+	+	+	−		+	+	−	−	−
XI	24 hrs.	78 (crude)	+	+	+	+	+		+	−	−	−
XII	24 hrs.	77 (crude)	+	+	+	+	+		+	−	−	−

Reaction Condition

Table 3

Halogenated Acyl Ester Series, $CH_2(OCOC_{11}H_{23})CH(OH)CH_2(OR)$

No.	R	M. P. °C.	Calcd. C	Calcd. H	Found. C	Found. H
XIII	$CHCl_2CO$	175—178/10^{-2}mm.Hg.*	52.90	7.84	52.61	7.50
XIV	CH_2ClCO	50.0—50.5 145—155/10^{-2}mm.Hg.*	58.19	8.19	58.57	8.78

* Bath temperature.

No.	Reaction time	Yield%	Solubility: MeOH	EtOH	AcMe	Et_2O	AcOEt	$CHCl_3$	C_6H_6	Petr. ether	H_2O
XIII	24 hrs.	82	+	+	+	+	+	+	−	−	−
XIV	24 hrs.	68	+	+	+	+	+	+	−	−	−

Reaction Condition

Solubility

according to the method described in the literature.[3~5] The amino group was acylated first with methyl dichloroacetate and then one or both hydroxyl groups were esterified with long chain aliphatic acids or p-nitrobenzoic acid.

Since it has been observed that the acyl migration[6][7] takes place from the oxygen of the hydroxyl group to the nitrogen of the amino group in acyl derivatives of the aminopropanediol in an alkaline solution and vice-versa in an acid solution, the confirmation of the chemical costitution of the final compounds prepared was desirable. If the 2-hydroxyl group in the 1-acyl-amino-2, 3-propanediol and the 1, 3-hydroxyl groups in the 2-acyl-amino isomer were left free, the migration of the acyl group from the nitrogen of the amino group to the oxygen of the hydroxyl groups to the 2- and 1 or 3-posititions, respectively, would occur on treatment with phosphorus pentachloride. Therefore, the hydroxyl groups were acylated previous to the treatment with

(3) E. Abderhalden and E. Eichwald, *Ber.*, **47**, 2888 (1913).
(4) E. Schmidt and R. Wilkendorf, *ibid.*, **52**, 338 (1919).
(5) H. Schlenk and B. W. De Haas, *J. Am. Chem. Soc.*, **73**, 3921 (1951).
(6) Max Bergmann and S. Sabetay, *Z. physical. Chem.*, **137**, 47 (1924).
(7) Carlo G. Alberti, XII Int. Congr. Meeting in New York, Sept., 1951.

phosphorus pentachloride. 1-Dichloroacetamido-3-lauroyloxy-2-propanol was esterified with stearoyl chloride and the resulting product was treated with phosphorus pentachloride,[8] followed by deamination with nitrous acid to give 1-lauroyl-2-stearoylglycerol, which was then esterified with stearoyl chloride. The final product melted at 56.0~57.0°C. and showed no depression of its m. p. when mixed with an authentic sample (m. p. 54.0°C.[9]) prepared according to Fischer's method.[10] Similarly, deamination was carried out with 2-dichloroacetamido-1, 3-dilauroyloxypropane.

This procedure proves that no migration of the dichloacetyl group or no interchange of the haloacyl with other acylgroup has taken place. The preparation of 1-lauroyloxy-2, 3-distearoyloxy from 1-dichloroacetamido-3-lauroyloxy-2-propanol shows that the monoacylation of the primary alcohol has taken place during the acylation of the haloacylaminopropanediol. Therefore, it is reasonable to state that the rest of the compounds prepared possess the structures as indicated.

Experimental

dl-Dichloroacetamidopropanediol (I).—A mixture of 18 g. (0.197 mol) of 1-aminopropanediol (140~140.5°C./6~6.5 mm) and 30 g. (0.209 mol) of methyl dichloroacetate was refluxed on the water bath for 1½ hrs. The methanol formed was removed and the residue was washed by decantation five times with 30 cc. portions of petroleum ether and dried over conc. sulfuric acid paraffin in a vacuum desiccator to induce crystallization. The crude product was dissolved in ethyl acetate, the solution filtered, the solvent removed and the residue washed with petroleum ether. The yield was quantitative.

1-Dichloroacetamido-3-lauroyloxy-2-propanol (III).—To a mixture of 8 g. (0.039 mol) of dl-dichloroacetamidopropanediol, 30 cc. of chloroform and 4 g. of pyridine, cooled to zero degree, was added dropwise 8 g. (0.037 mol) of lauroyl chloride* under constant stirring. The reaction mixture was allowed to stand at room temperature for 24 hrs., acidified with 1/2 N sulfuric acid and extracted with ether. The ether extract washed with a 5% solution of sodium carbonate followed by water and dried over anhydrous sodium sulfate. It was then filtered and the residue obtained after removal of the solvent was allowed to stand at −18°C. to allow crystallization to take place. The crude product was dried in a vacuum desiccator over conc. sulfuric acid, and purified by recrystallization from absolute methanol. The crude product weighed 10 g. (71% of theoretical yield), and pure product melting at 70.5~71.0°C. weighed 6 g. (43% of theoretical yield). The compounds 1-dichloroacetamido-3-nonoyloxy-2-propanol (II) and 1-dichloroacetamido-3-*p*-nitrobenzoloxy-2-propanol (IV) were prepared by the similar method described above.

dl-1-Dichloroacetamido-3-isobutyroyloxy-2-propanol (V).—To a solution of 6 g. (0.029 mol) of dl-dichloroacetamidopropanediol and 3 g. of pyridine in 5 cc. of chloroform was added, under cooling, 3.5 g. (0.026 mol) of isobutyroyl chloride and allowed to stand at room temperature for 24 hrs. The reaction mixture was treated in the manner similar to the method described for the preparation of 1-dichloroacetamido-3-lauroyloxy-2-propanol. Since it was found to be a liquid compound, the crude product was extracted with ether, the solvent removed, the residue extracted with alcohol, and the residue obtained after removing the alcohol was subjected to high vacuum distillation.

The 1-dichloroacetamido-3-isovaleroyloxy-2-propanol (VI) was prepared similarly.

1-Lauroyloxy-2, 3-distearoyloxypropane.—For the confirmation of the structure of 1-dichloroacetamido-3-lauroyloxy-2-propanol, one gram (0.0026 mol) of 1-dichloroacetamido-3-lauroyloxy-2-propanol was dissolved in a mixture of 10 cc. of chloroform and 2.5 g. of pyridine, the resulting mixture treated, under cooling, with 0.85 g. (0.0028 mol) of stearoyl chloride and the reaction mixture allowed to stand for 2 days. The subsequent treatment of the reaction mixture was carried out in the manner similar to the method described previously. The pure compound melted at 66~67°C.

The compound thus obtained was treated with phosphorus pentachloride according to the method described in the literature[5] to obtain the hydrochloride salt of 1-amino-2-stearoyloxy-3-lauroyloxypropane. The product was then deaminated with nitrous acid to give 1-lauroyl-2-stearoyl glycerol, which was then esterified with stearoyl chloride in the presence of pyridine. The purified triglyceride melting at 56.0~57.0°C. showed no depression of its melting point when mixed with the sample prepared according to Fischer's method.[10] (Reported m. p. 54.0°C.[9])

The total amount of lauric acid obtained by hydrolysis of 1-dichloroacetamido-3-lauroyloxy-2-propanol with 0.1 N sodium hydroxide was found quantitative.

2-Dichloroacetamidopropanediol (VII).—2-Aminopropanediol[5] was treated with methyl dichloroacetate in the manner described for the preparation of the dl-dichloroacetamido isomer. The crude product was purified once from a mixture of methanol and petroleum ether and then from absolute alcohol, m. p. 143.5−144.0°C. The yield was quantitative.

(8) Max Bergmann, E. Brand and F. Dreyer, *Ber.*, **54**, 935 (1921).

(9) B. F. Daubert, *J. Am. Chem. Soc.*, **66**, 291 (1944). Daubert prepared this compound by the reduction of 1-lauroyloxy-2, 3-dielaidoyloxypropane.

(10) E. Fischer, *Ber.*, **53**, 1589 (1920).

* Lauric acid used in this experiment was a c. p. grade of Matheson product.

2-Dichloroacetamido-1, 3-dilauroyloxypropane (IX).—A solution of 1.2 g. (0.0060 mol) of 2-dichloroacetamidopropanediol in a mixture of 30 cc. chloroform and 10 g. of pyridine was treated, under cooling, with 1.8 g. (0.0082 mol) of lauloyl chloride, the reaction mixture allowed to stand for three days, and treated in the manner described for the preparation of 1-dichloroacetamido-3-lauroyloxy-2-propanol. Compounds 2-dichloroacetamido-1, 3-dinonoyloxypropane (VIII), 2-dichloroacetamido-1-*p*-nitrobenzoyloxy-3-propanol (X), 2-dichloroacetamido-1, 3-dipalmitoyloxypropane (XI),* 2-dichloroacetamido-1, 3-distearoyloxypropane (XII),* were prepared according to the method mentioned above.

1-Chloroacetyl-3-lauroyl glycerol (XIV).—A solution of 4.5 g. (0.016 mol) of monolaurin (m.p. 62~63°C)[10] and 1.5 g. of pyridine in 15 cc. of chloroform was treated, under cooling, with 2.5 g. (0.022 mol) of monochloroacetyl chloride and the resulting reaction mixture was worked up as described previously. The product was taken up in ether, the solvent removed, and the residue subjected to high vacuum distillation.

Compound 1-dichloroacetyl-3-lauroyl glycerol (XIII) was prepared in the similar manner.

1, 3-Dilaurin.—Upon treatment of compound 2-dichloroacetamido-1, 3-dilauroyloxypropane with phosphorus pentachloride followed by nitrous acid, as described for the 1-compound, 1, 3-dilauryl glycerol, m. p. 56~57°C. was obtained. This product showed no depression of its melting point when mixed with the sample (m. p. 56~57°C.) prepared according to the method of Daubert[11] (reported m. p. 58°C.). The hydrolysis of 2-dichloroacetamido-1, 3-dilauroyloxypropane with 0.1 N NaOH gave quantitative recovery of lauric acid.

* Palmitic and stearic acids used were c. p. grades obtained from the "Delta Chemical Works", m. p. 61-62°C and 68-69°C, respectively.

Summary

Derivatives of 1-aminopropanediol, 2-aminopropanediol and the halogenated acyl esters of glycerol have been prepared. The amino group has been acylated with haloalkylacyl group and one or both hydroxyl groups with aliphatic acids of various chain lengths. Preliminary experimental results have shown that these compounds exhibit bacteriostatic activity in vitro against mycobacterium tuberculosis, avian. The chemical constitution of the isomeric products, the 1-amino and 2-amino derivatives, has been confirmed. The preparation of the optical active forms of the aminopropanediols are now in progress.

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(11) B. F. Daubert, *J. Am. Chem. Soc.*, **66**, 289 (1944).

LETTER

Diallylsilanediol, $(CH_2\text{-}CH\text{-}CH_2)_2Si(OH)_2$

Rokuro ŌKAWARA, Kōhei HASHITANI and Takeo WATASE

(Received April 25, 1953)

Organosilanediol is an interesting compound in the study of silicones. While saturated silanediols have been described in various papers, unsaturated silanediols have not been previously reported. Recently Frish, Goodwin and Scott[1] prepared a series of organosilanediols which have one unsaturated and one saturated hydrocarbon radical on the same silicon atom. But the one which has two unsaturated hydrocarbon radicals on the same silicon atom has not been prepared. We wish now to report on diallylsilanediol which has been prepared directly from diallyldichlorosilane with a similar principle as that of Lucas and Martin.[2]

In a three-necked 2 l.-flask, an efficient stirrer and two dropping funnels were inserted in each neck. As a hydrolyzing mixture, saturated sodium chloride solution (270 g.) with an excess of solid sodium chloride and ethyl ether (400 cc.) were used. Redistilled (30 g.) diallyldichlorosilane (*Anal.* Cl: Calcd. 39.2,

(1) K. C. Frisch, P. A. Goodwin and R. E. Scott, *J. Am. Chem. Soc.*, **74**, 4584 (1952).

(2) G. R. Lucas and R. W. Martin, *J. Am. Chem. Soc.*, **74**, 5225 (1952).

Found 39.3) prepared by the direct method was diluted with ethyl ether (200 cc.) and 1 N-sodium hydroxide solution were placed in each dropping funnel. By using methyl orange as indicator the two solutions were added differentially to the hydrolyzing mixture with vigorous stirring. During the course of addition the temperature of the mixture was kept below 4°C. and the color change of methyl orange was carefully controlled between slight red and orange, because *p*H of the mixture has a great influence on the yield. Sodium chloride was added at a time when the solid disappeared from the hydrolyzing mixture.

After the addition, the ether layer was separated and completely dehydrated on sodium sulfate. Then ether was distilled off on a water-bath below 40°C., or better aspirated off. The product, oily matter and crystalline solid were washed with a little quantity of petroleum ether (yield 21 g., 87% of the theory). A sample for analysis was recrystallized from ethyl ether, m. p. 81°C., d^{10} 1.105. *Anal.* Calcd. for $C_6H_{12}O_2Si$ (144.2): C, 50.09; H, 8.57; Si, 19.38; hydroxyl, 23.9%. Found: C, 49.96; H, 8.39; Si, 19.44; mol. wt. 147 (in dioxane), 144.9 (from X-ray analysis); hydroxyl (Karl Fischer) 22.5%. Iodine value I_0: Calcd. 352, Found 355.*

Details on the preparation and properties of this compound will be reported later.

We thank Mr. M. Kakudo for the X-ray analysis and Takeda Yakuhin Kōgyō Laboratory for the determination of carbon and hydrogen.

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* The high iodine values (I_e) proportional to the excessa mount (e) of Wijs reagent were observed. The value I_0 was obtained from the several I_e values by extrapolating graphically when $e \to 0$.

The Formation of Cycloöctatetraene in the Thermal Polymerization of Acetylene

By Zenichiro KURI

(Received April 28, 1953)

The success of the detection of cycloöctatetraene (C. O. T.) in the photopolymerization products of acetylene and a theory on the mechanism of its formation have already been reported.[1] Extending this to the thermal polymerization, the author found C. O. T. here also in the products. Reppe,[2] too, supposed that it might exist in the thermal polymerization products, but he failed to demonstrate it.

The apparatus, the analysis of C. O. T., and others were the same as in the former experiment, except that an electric furnace (12 cm. in length) was used in place of a mercury lamp. The linear flow rate of acetylene through the reaction tube was maintained at 2.6 cm. /

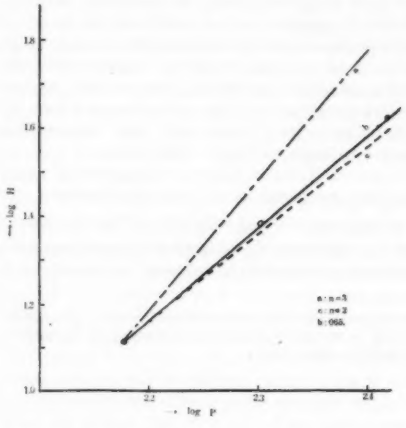

Fig. 1.—H: Rate of formation of C·O·T.
P: Pressure of acetylene.

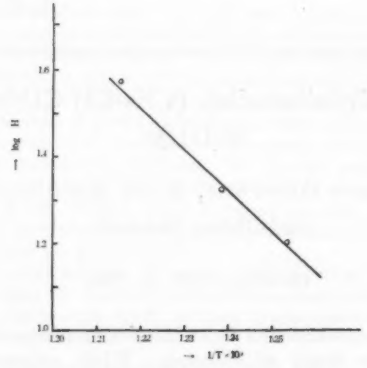

Fig. 2.—H: Rate of formation of C·O·T.
1/T: Reciprocal of the temperature °K.

(1) Z. Kuri and S. Shida, This Bulletin, **25**, 116(1952).
(2) J. W. Reppe, Acetylene Chemistry (P. B. Report 18852-s) p. 151 (1945).

sec. (A) The pressure was changed from 150 to 250 mm. Hg. The temperature was kept constant at 550°C. Fig. 1 shows the logarithm of the rate of C. O. T. formation (expressed in the height, mm, of the polarographic diffusion current) vs. the logarithm of pressure of acetylene, where $n=2$ and $n=3$ means the second and the third order reaction, respectively, in respect to acetylene. The slope indicates the reaction to be practically of the second order. (B) The temperature was changed from 525° to 550°C. The pressure of acetylene was kept constant at 250 mm.Hg. Fig. 2 shows the logarithm of the rate of C. O. T. formation vs. the reciprocal of the temperature. From the slope one gets the activation energy of C. O. T. formation, 44.3 Kcal. Details of the experiment and the reaction mechanism will be published later. The author is grateful to Dr. S. Shida for his helpful discussion.

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